

METALLURGIA

THE BRITISH JOURNAL OF METALS
INCORPORATING THE "METALLURGICAL ENGINEER."

MAY, 1951

Vol. XLIII No. 259

Non-Ferrous Productivity

PRIOR to their departure for the United States last year, the Productivity Team representing the Wrought Non-Ferrous Metals industry spent approximately a month in touring a representative selection of factories in Britain. This enabled the team to obtain a fairly extensive idea of what was being done on the British side and to discuss their everyday problems with their opposite numbers in other works to the benefit of all concerned. By these preliminary visits, the team feels that the seed has been sown for a co-operative effort by British manufacturers and the first general recommendation in its recently published Report* is that British industry should set up a permanent organisation for sectional productivity teams to survey periodically the British non-ferrous metals industry, covering the main processes: melting and casting, rolling, extrusion, wire-drawing, and tube drawing. Such teams need consist only of a few practical and technical men from the industry, the frequency of visits, whether one, two or three years, being fixed by that section of the industry concerned. In the same way, the extent to which the reports of such teams should be distributed would also be left to the particular section of the industry involved. That such a procedure could be of immense benefit to the industry, in improving its efficiency, cannot be doubted and it is to be hoped that the recommendation will not be allowed to "lie on the table," but that steps will be taken to hammer out a practical scheme for implementing it.

No one who has read a number of these Productivity Reports can fail to have been impressed with the similarity in principle, if not in detail, of the earlier sections dealing with the non-technical aspects of the various industries visited. Reference is frequently made to the way in which workers and managements approach the question of increased productivity, the position being admirably summed up by the following extract: "The attitude of employer and employed in America to increased productivity is the same everywhere. Their viewpoint is that greater productivity means more output per man-hour, with an ultimate reduction in cost. This should mean cheaper commodities to the public, with a consequent increase in spending power and a greater demand for those commodities. As far as the team can ascertain, it works. This aspect might be borne in mind by any in our industry who fear that the adoption of our recommendations may cause redundancy." There is no doubt that the attitude of the workers and their trade unions to such things as shift-working, time study, rate fixing, incentives, new methods, etc., is vastly different from that prevailing in Britain. The main object of the American unions is to get the best remuneration possible

for the worker and, on the whole, organised labour is prepared to leave management to manage, although it has time-study experts available for checking rates.

On the economic side there is much to be said for simplification of product so that large production runs can be made without interruption. Every effort should be made, therefore, to encourage the use of standard sizes and standard compositions, or perhaps we should say, to discourage the use of special sizes and compositions. It is American practice to penalise more heavily than we do non-standard material and small lots.

Considerable attention is given to process planning in the United States, and the team feels that this is an essential factor in improving productivity. The American planning supervisor and his staff are responsible for arranging the programme of work through the mill, receiving the orders from the sales department and arranging for their production in the most economical manner.

Again, in costing, the forward outlook is in evidence, and almost all the firms visited have adopted the basic method of standard costing with budgetary control. Although the installation of a standard costing system was a long and difficult procedure in all cases, the practical value of the results justified the effort. In discarding the more historical methods of costing, managements have given expression to the view that costs, to fulfil their true function, must give a usable and useful guide for the present and future, rather than an historical survey of the past.

In the U.S. works, any time lost at a machine in waiting for work, or for other causes, is regarded as a crime, and the team recommends the application of work study, paying particular attention to the operation of each machine to see that it is operating at the highest possible efficiency rate. This is largely dependent on the transfer of material from one operation to the next, the suitability of the material to enter the machine, and the siting of the machine. While advocating such studies and the adoption of planning methods, the Report considers that modern developments in plant call for a cautious approach by British manufacturers, since they are all directed towards large-scale production.

Naturally a considerable part of the report concerns the technical aspects of production and without going into details it may be said that there is much in American casting, rolling and tube-drawing technique and practice which it would be to the advantage of this country to follow. In wire-drawing there is perhaps very little difference in production efficiency, whilst in the extrusion process, British practice seems to be more efficient in a technological sense than American.

In conclusion the Report considers that what has been achieved in large and small American works, largely by improvisations without heavy capital expenditure, can be repeated here and, in the opinion of the team, the primary responsibility for increased productivity rests with management.

* Copies of the Report, price 4s. 6d. (post free), may be obtained from the British Non-Ferrous Metals Federation, 132, Hagley Road, Birmingham, or the Anglo-American Council on Productivity, 21, Tophill Street, London, S.W.1.

Canadian Aluminium Projects

DECISIONS to launch immediately a new expansion programme in the Canadian aluminium industry, involving the first stage of a vast new integrated aluminium development in the remote areas of British Columbia, and construction of another major hydro-electric power plant in the Province of Quebec, were announced recently by Nathanael V. Davis, President of Aluminium, Ltd. In a speech to the Annual Meeting of Aluminium, Ltd. shareholders in Montreal, Mr. Davis said that the Canadian developments would be undertaken by the company's subsidiary, Aluminium Company of Canada, Ltd., while operations to provide the needed intermediate material alumina, derived from bauxite ores, would be expanded in the Caribbean area.

Total capital expenditure involved in the programme presently planned is two hundred and twenty million dollars of which one hundred and sixty million dollars will be the estimated cost of the integrated first stage British Columbia development, including the required alumina facilities. The remaining sixty million dollars is the estimated cost of a new two hundred thousand horse-power hydro-electric plant at the Chute Savanne on the Peribonka River in the Saguenay district of north-eastern Quebec, together with new aluminium ingot facilities to be built in the district.

The announcement brought to an end a lengthy period of investigation and speculation concerning the possible start of aluminium production in the Tweedsmuir Park area of British Columbia. As a result of engineering surveys conducted over several years, it has been determined that low-cost electric power on which the industry depends can be obtained by a major engineering project in the undeveloped area four hundred miles north-east of Vancouver. It will be done by utilising the waters of a chain of interior lakes and dropping the water through a ten mile tunnel beneath the coastal mountains to a powerhouse inside the mountain two thousand five hundred feet below the level of the lakes. The aluminium smelting plant and a new town to house the working force will be built near the tidewater Indian village called Kitimat. Raw materials from the Caribbean and other areas will be brought to Kitimat by sea or railway spur, taking off from terrace, from the C.N.R. main line into Prince Rupert.

Expected increase in integrated Canadian aluminium productive capacity resulting from the two province expansions scheme is one hundred and fifty thousand metric tons (three hundred and thirty million pounds) per year, bringing total usable integrated capacity over the five hundred and fifty thousand ton mark. Of the new increase in capacity, approximately eighty to one hundred thousand metric tons will be located in British Columbia, involving the installation of the necessary generating capacity. From the outset, however, the tunnels beneath the mountains and a powerhouse cavern sufficient for eight hundred thousand horsepower will be excavated, thereby providing the basis for further rapid expansion.

The company is already embarked on a forty-five million dollar programme to develop an initial site on the Peribonka River called Chute du Diable (Devil's Falls) to produce two hundred thousand firm horse-power and support approximately forty-five thousand tons of annual aluminium production. The decision to build additionally the Chute Savanne powerhouse will permit

still further increased aluminium output in the Saguenay area commencing one year from now, thereby assisting the company to meet the strong near term demand which the previous production and expansion programme could not fill. The British Columbia scheme on the other hand will require more than three years of construction and is based on long range considerations which led the company to prepare itself to maintain at least its relative position as a traditional supplier in international markets.

Although the annual rate of expenditure and the estimated completion date will depend upon the construction schedule adopted, it is currently planned to proceed without delay under a schedule which, if maintained, will bring in production of the first aluminium in British Columbia in 1954. Estimated expenditures this year under the programme now in effect will be twenty-three million dollars. It should, however, be remarked that if at any time there are indications that the additional output will not find markets the construction schedule will be lengthened to coincide with the estimates of future requirements and with the resources available to the company.

The combined developments at Chute Savanne and British Columbia, which will increase usable integrated ingot capacity by 150,000 metric tons per annum, will call for a total capital expenditure of approximately two hundred and twenty million dollars. Prolonged study has been given to the financing of the combined programme. Having regard for the funds now in hand and assured, the company believes, under present estimates, that the financial arrangements for the combined developments have been substantially completed. The company further believes that such additional financing as may be required can be handled on a normal basis.

Die Casting Productivity Team

On the 8th of May, a team, formed under the auspices of the Anglo-American Council on Productivity, with E.C.A. technical assistance, to study die casting, set out for the U.S.A. Its seventeen members have been drawn from the zinc and aluminium pressure and gravity die casting industries through the co-operation of the Zinc Alloy Die Casters' and the Light Metal Founders' Associations.

The manufacture of castings in permanent and semi-permanent moulds has been developed to a far greater extent in the U.S. than in Europe, and industry there makes greater use of these highly productive methods. It is believed that not only is die casting more widely used in the U.S. than in the U.K., but also that greater productivity is achieved in the manufacture of similar components. During its visit, the team will be engaged primarily in seeking the reasons for these two differences.

The team leader is Mr. C. R. LYONS of the Imperial Smelting Corporation, Ltd., which manufactures most of the zinc die casting alloy consumed in the U.K. He is assisted by Mr. H. E. ROBINSON, Foundry Manager of Sterling Metals, Ltd., who is acting as leader on the gravity die casting side. As with all other productivity teams, the members are drawn equally from management, technical and workshop levels. In addition, there are two secretaries. Mr. F. CARPENTER of Sterling Metals, Ltd. on the light alloy gravity die casting side, and Mr. A. K. PARKER of the Zinc Development Association on the zinc alloy pressure die casting side.

Zirconium

Production, Properties and Alloys

By G. L. Miller, Ph.D., B.Sc., A.R.I.C., M.I.Chem.E.

(Research Manager, Murex, Ltd., Rainham)

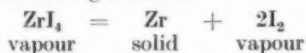
The extraction metallurgy of some of the "newer metals" is in striking contrast with that of the long established materials as will be seen from the description of the methods used to obtain zirconium from its ores. In view of the fact that commercial production, albeit on a limited scale, has recently commenced in this country, it was felt that a review of manufacturing methods, along with an outline of the properties of the metal and its alloys, was opportune.

THE development of zirconium has taken place in a number of distinct phases. The first phase covered a period of about a hundred years, from the production of zirconium by Berzelius, who made zirconium metal powder which contained too many embrittling impurities to make it useful, to the work done by van Arkel and others in developing small scale production of pure ductile metal by the Iodide method. This for a time was the accepted technique but as the production was very limited the zirconium was expensive and it remained a comparatively rare metal. The next phase was the introduction of the technique which has since become known as the Kroll process; development was rapid, and in a few years the knowledge gained from a laboratory scale unit had been applied to a plant producing about 600 pounds of metal per week. Simultaneously, work was in progress in an attempt to improve the Iodide process, but this did not proceed at the rate of its rival's development. The present phase is rather complex; improvements have been suggested for both the Iodide and Kroll processes and, in addition, claims have been made for an electrolytic process, although earlier investigators rejected this method as being unsuitable.

In considering the development of zirconium, it is necessary to include some of the work that has been done on its sister metal, titanium, particularly as novel methods for improved production of this metal have been suggested recently.

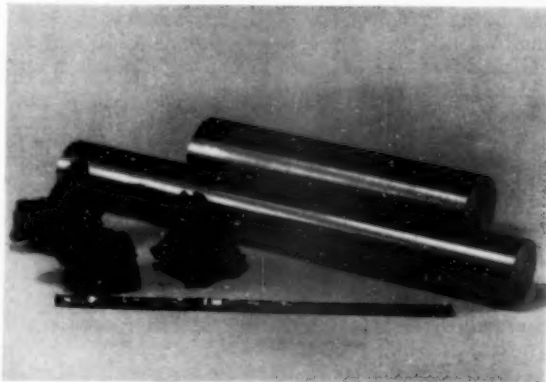
Iodide Process

The van Arkel or Iodide process is very simple, as is shown by the following formula:—



All that is necessary to achieve this decomposition is heat, and in the Iodide technique the temperature necessary for the reaction is generated by passing current through a thin wire or filament of zirconium. This not only provides the heat, but also leads to the production of a solid rod of zirconium by the gradual deposition of the zirconium on the wire.

The original work was carried out in glass vessels which had to be evacuated because hot zirconium reacts avidly with oxygen and nitrogen and the oxide and nitride so formed embrittles the metal and render it unworkable. It is this property of combining with the common gases that delayed the production of zirconium,



Zirconium sponge and machined ingot produced by the Kroll process, with zirconium rod produced by the Iodide process in the foreground.

and still makes its production difficult and expensive.

The zirconium tetraiodide required in the process was produced by the action of iodine vapour on heated impure zirconium metal, obtained by the reduction of zirconium dioxide by calcium. This crude metal contained considerable quantities of oxide which was left as a residue when the zirconium tetraiodide vaporised. The glass vessel which contained the heated filament also contained the crude zirconium, and, when the iodine was introduced, the metal was sufficiently hot to react and form tetraiodide vapour, which then contacted the molten filament and was decomposed into its elements, the regenerated iodide vapour returning to react with more crude zirconium. As will be seen, the method possesses many virtues and so long as the necessary precautions were taken ductile metal was obtained. The first development which was proposed was the replacement of the glass vessel by a metal one, to permit the scale of the operations to be enlarged. Eventually, after some difficulties, an alloy was found which could withstand the corrosive action of the iodide vapour, but larger scale operations introduced new problems. It was known that, while the filament temperature had to be maintained above a certain level, it was also essential to avoid overheating the crude zirconium, in order to prevent the formation of zirconium di-iodide which would not vaporise under the existing conditions and could thus bring the whole cycle to a complete stop. Arrangements

had to be made, therefore, to keep the crude zirconium at a suitable temperature by cooling the outside of the vessel. Investigations are in progress to overcome such difficulties and, in addition, efforts are being made to overcome the obvious drawback of having to make the crude metal as an intermediate. Suggestions have been made to use either an alloy of zirconium, such as aluminium-zirconium, or the carbide, which can then be converted to pure tetraiodide by treatment with iodine vapour at an elevated temperature.

Kroll Process

As in the case of the Iodide process it is possible to illustrate the main reaction by a simple formula:—



The main difference, which is immediately obvious, is that in the case of the Iodide method the zirconium is obtained free from the other product of the reaction, whereas in the above reaction the zirconium is produced simultaneously with liquid magnesium chloride, and the final product is an intimate mixture of zirconium and solid magnesium chloride.

The zirconium tetrachloride is usually produced by the chlorination of a zirconium-carbo-nitride, formed by the carburisation of zircon (zirconium silicate) in an arc furnace. The chloride so produced contains some iron and silicon and appreciable quantities of oxide; in addition, it is in a light flocculent state which makes it difficult to prevent the absorption of large quantities of moisture from the atmosphere.

Zirconium tetrachloride is very hygroscopic and any water which is absorbed results in the formation of hydroxide, leading eventually to the presence of oxide in the reduced metal. It is, therefore, essential, if ductile metal is to be obtained, that the oxide it contains should be eliminated and, as a preventative measure, the chloride must not be allowed to absorb moisture. There is no difficulty in removing the iron, silicon and oxide by resubliming the crude chloride in an atmosphere of hydrogen. In the Kroll process, the crude chloride is heated in a nickel crucible in a sealed stainless steel vessel with a special cover incorporating a cooled coil condenser. The temperature of the whole apparatus, except the condenser, is raised above the sublimation temperature of the zirconium tetrachloride. The coil is controlled at a temperature just low enough to cause condensation of the chloride; this results in the formation of a dense block of chloride which does not absorb atmospheric moisture readily.

The purpose of the special cover just described is not only to ensure the collection of the purified chloride in a dense form, but also to facilitate the removal of the material to the next stage of the process, which is the reduction. The reduction takes place in a vessel similar to that used for the purification and densification. A crucible containing magnesium ingot is placed in the bottom of the vessel and the cover, together with its condenser loaded with zirconium tetrachloride, is lowered into the vessel and sealed. The vessel is evacuated and refilled with argon and the magnesium heated to above the melting point of magnesium chloride, so that when the zirconium tetrachloride is vaporised it reacts to form zirconium and molten magnesium chloride. The product is an intimate mixture of metallic zirconium and magnesium chloride containing a little magnesium metal. The crucible containing this charge is inverted

and charged into a vertical steel retort where it is heated in vacuum until all, or nearly all, the magnesium chloride is removed and, at the same time, the free magnesium is also vaporised from the charge. The residue is zirconium metal in a sponge-like mass which is very reactive towards air; it must be conditioned by gradual addition of air to the retort before exposing to the atmosphere.

The metal sponge has now to be converted to solid metal by melting in vacuum or in an inert atmosphere. Kroll used a split tube graphite resistor furnace with a carbon crucible to contain the charge. Carbon was used because zirconium reduces all the normal refractories, and although a slight carbon pick-up occurs it is not very detrimental to the final product. It is possible to produce sound ingots by melting the zirconium in an argon arc furnace, the metal being supplied either as a consumable electrode or as pieces of sponge which are melted by the arc struck from a tungsten tipped electrode. In both cases the molten metal is collected in a water-cooled copper crucible. The final process is the conversion of the ingot metal to sheet, rod, wire, etc. The working of the metal is again complicated by its reactivity towards oxygen, and nitrogen when it is heated, and it is necessary to protect it by enclosing in a steel sheath.

The main improvement which has been proposed for operating the Kroll process is the carrying out of the purification and reduction simultaneously. The apparatus, which is described by Kroll and others, consists of two main vessels connected by a short piece of heated pipe. In one vessel the crude zirconium chloride, after heating in hydrogen at a low temperature to fix the iron and remove the silicon, is vaporised and passed into the reduction vessel by means of the connecting pipe. In the reduction vessel magnesium is melted in a special crucible fitted with a salt-tapping device. When all the available magnesium has reacted, the bulk of the molten magnesium chloride formed is drained from the crucible by the tapping device and a fresh charge of molten magnesium introduced into the crucible and the reduction continued. By this means it is possible not only to eliminate a step in the process but also to build up a much larger charge of zirconium in the reduction crucible and so increase the capacity of the sales removal retort.

The removal of the magnesium chloride in the molten state has already been reported in the production of titanium. Titanium, as stated earlier, is the sister metal to zirconium, it is in fact, the elder and more popular sister, and so its progress is in many cases indicative of that of zirconium. Titanium tetrachloride is a liquid, and its addition to the reduction vessel containing the molten magnesium is much simpler than in the case of the solid zirconium tetrachloride. There is no separate container for the molten magnesium in the case of titanium; the reaction takes place in the bottom of the main vessel, thus simplifying the tapping of the molten magnesium chloride. A drain pipe at the bottom edge of the reduction unit is sealed by a solid plug of magnesium chloride which is prevented from melting by a water-cooled tube pressing on the end of the block. When necessary, the cooling tube is withdrawn from the plug of magnesium chloride which melts and allows the bulk of the molten magnesium chloride to be drawn from the reaction vessel.

As in most metallurgical operations, attempts have been made to devise a continuous process. One method which has been tried on a small scale, and claimed to be

feasible involves the continuous addition of molten magnesium and titanium tetrachloride to a chamber where reduction takes place at a temperature about 850° C. The molten reaction product flows continuously to an arc furnace where the titanium is melted to form an ingot and the unreacted magnesium and magnesium chloride are vaporized. It is suggested that the titanium ingot could be removed continuously.

Another ingenious process which has been proposed for the production of titanium and which, if successful, could be applied with modifications to zirconium, is the reduction of titanium tetrachloride by hydrogen in an electric arc furnace. The process has been tested on a very small scale. The arc was held in H₂-TiCl₄ vapour mixture but unfortunately after a few minutes operation the experiment had to be stopped. The results indicated that some reduction had taken place and the investigators see no reason why the process should not be scaled up to a large production unit.

Electrodeposition of Zirconium

Many attempts have been made to produce zirconium by electrolysis of aqueous and non-aqueous solutions, and fused-salt baths, but all investigators reported failure. Recently an investigation was made using numerous aqueous and non-aqueous solutions but none of the solutions used gave a weighable electrodeposit of pure zirconium, although some solutions gave thin cathode deposits which contained zirconium and iron. In view of these results it is surprising to learn of a recent claim, in a Japanese patent, for the successful electrodeposition of zirconium. The patent describes the electrodeposition by the use of a solution made by adding an excess of ammonium carbonate to a solution of zirconium oxychloride (ZrOCl₂). This solution is said to eliminate the usual difficulty caused by precipitation of zirconium hydroxide.

Some Properties of Zirconium

The properties of zirconium have been described in detail in various journals but it will be useful to give a general outline of the main characteristics of the metal. The outstanding property of zirconium is its resistance to chemical corrosion; in many respects it is similar to tantalum. Concentrated hydrochloric and phosphoric acids have a slight attack, while concentrated nitric acid has no effect. Concentrated sulphuric acid attacks readily but the diluted acid has little effect. While tantalum is readily attacked by alkalis, zirconium is outstanding in its resistance and even fused caustic has no effect.

The figures shown in Tables II and III should only be used as guides, as there are many factors which may affect the result and it is always better to make a test under conditions similar to those for which the metal is required.

The corrosion resistance properties of zirconium combined with good mechanical strength will make it a useful constructional material for chemical engineers. It has been tested for surgical repair parts and reports indicate that it is very suitable for this purpose.

The activity of zirconium toward oxygen and nitrogen make it a very excellent getter and it may become important in the electronic industry.

Recent U.S. reports suggest that zirconium will be used as a constructional material for atomic energy projects because of its low neutron absorbing capacity.

TABLE I.—PHYSICAL PROPERTIES OF ZIRCONIUM.*

Atomic	(1) Atomic number 40 (2) Atomic weight 91.22 (3) Lattice type H.C.P. Below 880° C. a ₀ 3.22 Å c ₀ 5.12 Å c/a 1.589 B.C.C. above 880° C. 3.61 Å
Mass	Density at 20° C.; 6.52 g./cc.
Thermal	(1) Melting point 1,860° C. (3,380° F.) (2) Linear coefficient of expansion. 20 — 200° C. 5.4 × 10 ⁻⁶ per °C. 20 — 400° C. 6.9 × 10 ⁻⁶ 20 — 700° C. 8.9 × 10 ⁻⁶ (3) Specific heat 0 — 100° C. 0.068 cal./g. (4) Thermal conductivity at 50° C. in C.G.S. units 0.04 c. (5) Vapour pressure No data (B.P. ca. 3,000° C.)
Electrical	(1) Electrical resistivity 39 × 10 ⁻⁶ ohm-cm. (iodide Zr) (2) Electrical conductivity % I.A.C.S. 4.1 (iodide Zr) (3) Temperature coefficient of resistivity 0.004 C ⁻¹ (iodide Zr) (4) Super conducting at 0.7° K. (5) Electrochemical equivalent 0.2363 mg./coul.
Thermionic	(1) Work function 4.1 electron volts (2) Photoelectric threshold, long wave limit 3,200 Å
Magnetic	(1) Diamagnetic, susceptibility - 0.45 × 10 ⁻⁶ at 18° C.

* "Zirconium Metal as of 1949" by R. I. Jaffee, Battelle Memorial Institute, Columbus, Ohio.

TABLE II.—CORROSION RESISTANCE OF ZIRCONIUM.*

Agent	Concentration	Room Temperature Inches per year	100° C.
Atmosphere	—	No attack	No attack
Acids			
HCl	5%	No attack	No attack
HCl	Conc.	0.0001	0.0002
H ₂ SO ₄	10%	0.0002	0.0007
H ₂ SO ₄	Conc.	—	Attacked
HNO ₃	10%	0.00001	0.00003
HNO ₃	Conc.	0.00001	0.00005
Aqua regia	—	Attacked slowly	Attacked
HF	—	Rapid attack	—
H ₃ PO ₄	10%	0.00001	0.00005
H ₃ PO ₄	Conc.	0.00004	Attacked
Bases			
NaOH	10%	No attack	0.00002
NaOH	50%	—	0.00017
NaOH	Fused	No attack	—
KOH	10%	0.00002	No attack
KOH	Fused	Slight attack	—
Others			
KNO ₃	Fused	Attacked	—
Cl ₂ water	—	Attacked	—
FeCl ₃ solutions	—	Attacked (embrittled)	—
NaCl	20%	Attacked (embrittled)	Slight tarnish

* "Zirconium Metal as of 1949" by R. I. Jaffee, Battelle Memorial Institute, Columbus, Ohio.

TABLE III.—ACID CORROSION RESISTANCE OF TANTALUM, COLUMBIUM, ZIRCONIUM AND TITANIUM.*

Solution	Temp. °C.	Test period days	Corrosion rate, Inches/Year			
			Tantalum	Columbium	Zirconium	Titanium
HCl, 18%	19-26	36	0.00000	0.00000	0.00009a	0.0445
HCl, conc.	19-26	36	0.00000	0.00012	0.00008	0.698
HCl, conc.	110	7	0.00000	0.004 b	0.01875	Not tested
HNO ₃ , conc.	19-26	36	0.00000	0.00000	0.00000	0.00005
HNO ₃ , 2HCl	19-26	35	0.00000	0.00002	Very soluble	0.00021
HNO ₃ , 2HCl	50-60	1	0.00000	0.001	Very soluble	Not tested
H ₂ SO ₄ , 50%	19-26	35	0.00000	Not tested	0.00000	0.0021
H ₂ SO ₄ , conc.	19-26	36	0.00000	0.00002	Very soluble	0.0468
H ₂ SO ₄ , 20%	95-100	4	0.00000	0.00002	0.00018	Not tested
H ₂ SO ₄ , conc.	145	30	0.00000	0.18 a	Very soluble	Very soluble
H ₃ PO ₄ , 35%	19-26	36	0.00000	0.00002	0.00002b	0.00675
FeCl ₃ , 10%	19-26	36	0.00000	0.00000	0.00042c	0.00003

(a) embrittled; (b) tarnished; (c) uneven corrosion.

* "Acid Corrosion Resistance of Tantalum, Columbium, Zirconium and Titanium" by D. F. Taylor, Fansteel Metallurgical Corporation, North Chicago.

Zirconium can be melted under vacuum, ingots of reasonable size being produced, and, if suitable precautions are taken to prevent undue oxidation, the ingots

TABLE IV.—MECHANICAL PROPERTIES OF ZIRCONIUM METAL.^a

Property	Unit	Hard drawn	Annealed at 790°C (1,450°F.)
Ultimate strength	p.s.i.	83,300	35,900
Yield strength 0-2% offset	p.s.i.	69,700	15,900
Proportional limit, 0-0.1% offset	p.s.i.	32,100	8,350
Elongation in 4 diameters	%	18-9	31-9
Modulus	p.s.i. × 10 ⁶	14.5	11-35
Hardness	Rockwell B	87.4	20.3

^a "Zirconium, and its Applications" by W. M. Raynor, *Mining and Metallurgy*, 1947, p. 284.

may be forged, rolled or swaged to produce many useful forms such as sheet, rod, and wire.

Welding may be performed by the spot welding technique or by argon arc fusion welding. In the latter case the weld, while strong, is too brittle to permit working. Machining zirconium is a simple matter and, provided sharp edges are maintained to avoid work hardening, excellent results are obtained.

Sheet may be formed to many shapes, while spinning is being satisfactorily performed on a limited scale. Tube is not yet available but the ductility of the metal indicates its production is practicable. The main difficulty to be overcome in the case of tube production is the tendency for the metal to weld to the dies.

Alloys of Zirconium

Until recently very few systematic investigations of zirconium alloys had been made, and even the latest work has been limited because the investigators have studied the alloys for a particular application.

One of the most comprehensive investigations in zirconium alloys was carried out by the U.S. Bureau of Mines in co-operation with the U.S. Air Material Command to determine the suitability of zirconium alloys for high temperature applications. About 25 zirconium-rich alloy systems were investigated and data on preparation, fabrication, tensile properties, metallographic structures, constitution and heat resistance has been published (see Table V).

It is pointed out in the introduction to the report that the investigation was made possible by the developments in the production of zirconium metal. The alloys were made by melting the ingredients in graphite with suitable provisions to prevent oxidation.

It was found that the alloys with the best heat resistance at 1,200° F. have the poorest yield strength at this temperature and it is concluded that it is doubtful if any of the alloys can be classified as satisfactory for service at 1,200° F.

It was fully appreciated that carbon would be absorbed as a result of melting in graphite, but it was not expected that the contamination would be very great. The carbon content of Kroll's metal, melted in the split tube graphite resistor type of furnace, is usually from 0.10-0.15% and in one instance, when the metal was raised to 2,000° C. and maintained at this temperature for 20 minutes and allowed to cool in the graphite crucible, the carbon content of the metal was 0.106%. However, on remelting this ingot in a fresh crucible the carbon was raised to 0.245%. By repeating this operation a maximum carbon content of 0.35% was obtained. The physical properties of zirconium sheet produced from zirconium ingot containing 0.35% were determined and are shown in Table VI. It was concluded that the presence of 0.35% carbon in zirconium did not produce any deleterious effects upon the tensile properties of hot rolled sheet.

TABLE V.—SUMMARY OF THE PHYSICAL PROPERTIES OF ZIRCONIUM ALLOYS.^a

	Limit of addition, %	Forging limit of 850° C., %	Heat resistance ¹ at 650° C. (1,200° F.)	Yield strength ² p.s.i. × 1,000	
				21° C. (70° F.)	650° C. (1,200° F.)
Aluminum	19	2	C	96.3	24.6
Beryllium	5	—	C	—	—
Boron	5	—	C	—	—
Cerium	5	—	C	—	—
Chromium	10	10	B	79.3	14.9
Cobalt	16	7	B	59.1	10.3
Cobalt - 1/2 to chromium 1 to 5 Cr	4 Co	A11	C	76.2	10.5
Columbium	12	12	C	79.8	10.0
Copper	15	11	B	49.2	8.7
Copper ternary	5	—	A	—	—
Iron	60	5	A	60.1	7.0
Manganese	25	10	C	67.0	12.5
Molybdenum	10	8	C	136.0	14.7
Nickel	10	3	C	75.8	8.6
Silicon	5	3	A	78.6	12.7
Silver	10	10	A	59.7	12.9
Tantalum	20	15	C	92.2	16.5
Thorium	5	—	C	72.7	10.2
Tin	10	10	C	64.6	17.8
Titanium	90	A11	C	139.1	17.3
Tungsten	10	19	C	91.3	12.2
Vanadium	10	5	C	82.5	14.7
Zirconium	—	—	B	36	9.1

¹ A—weight gain less than 600 mg./sq. dm./day (m.b.).

B—weight gain 600 to 1,500 m.b.

C—alloy disintegrated in less than 24 hours.

² Highest yield strength in alloy series.

^a "A Preliminary Survey of Zirconium Alloys" by C. T. Anderson, E. T. Hayes, A. H. Roberson, and W. J. Kroll. Bureau of Mines Report of Investigations No. 4658, p. 3.

TABLE VI.—PHYSICAL PROPERTIES OF ZIRCONIUM SHEET CONTAINING 0.35% CARBON.^a

Con. condition	Yield strength 0-2% offset	Ultimate strength, p.s.i.	Elongation %	Reduction in area %	Rockwell hardness, B
Hot rolled at 850° C.	p.s.i.				
Heated in air 1 hr. at 500° C.	34,900	63,100	15.0	—	83
600° C.	35,300	60,600	14.0	—	82
700° C.	32,700	60,300	13.5	—	83
800° C.	34,200	60,800	14.4	—	82
Room temperature ²	40,300	69,200	15.0	20.37	85
650° C. (1,200° F.) ²	4,620	14,320	26.0	57.2	83

¹ U.S.B.M. data, 0.062 × 0.30 in. standard A.S.T.M. sheet tensile specimens.

² Wright Field data, standard A.S.T.M. 1-in. round specimens from rods swaged at 850° C.

^a *Ibid.*, page 10.

TABLE VII.—TENSILE PROPERTIES OF ZIRCONIUM-TANTALUM ALLOYS.^a

Nominal analysis	Testing temperature °C.	Yield strength 0-2% offset p.s.i.	Ultimate strength p.s.i.	Elongation %	Reduction in area %	Rockwell hardness
1	Room	51,500	82,800	20.5	40.68	90
5		73,000	110,200	17	35.67	99
10		92,200	124,800	9	15.31	101.5
15		84,400	118,800	19.5	33.87	101.5
1	650	9,680	21,770	53	79.5	—
5		17,210	33,400	36	70.4	—
10		16,420	34,900	35	73	—
15		16,450	36,900	29	34	—

^a *Ibid.*, page 39.

One of the most interesting groups of alloys in the series investigated is the zirconium-tantalum group, because although it was obviously useless as a heat resistant material it might be expected to be a very useful metal to resist chemical corrosion. The tensile properties of forged alloys containing up to 14.1% tantalum are shown in Table VII from which it will be seen that the properties obtained by the addition of 10% tantalum are remarkable.

TABLE VIII.—TENSILE PROPERTIES OF ZIRCONIUM-IRON ALLOYS.*

Composition		Testing temperature °C.	Yield strength 0.2% offset p.s.i.	Ultimate strength p.s.i.	Elongation %	Reduction in area %	Rockwell hardness B
Fe %	C %						
0-029	0-140	Room	48,900	81,600	20	47-29	86
0-45	0-169		51,900	72,100	16-5	28-66	85
0-66	0-23		62,900	89,000	19	37-07	92
1-13	0-18		46,100	78,800	15-5	29-86	87
1-73	0-15		47,700	75,800	4	2-40	90-5
2-9	0-08		55,400	92,900	7	2-88	96
5-16	0-15		60,100	75,800	2-5	2-40	99-5
0-029	0-140	650	9,250	17,460	43	79	—
0-45	0-169		3,710	12,360	81	74	—
0-66	0-23		6,070	17,430	75	86	—
1-13	0-18		4,380	15,730	888	89	—
1-73	0-15		6,980	20,530	87	92	—
2-9	0-08		6,170	21,560	75	83	—
5-16	0-15		6,700	23,310	51	62	—

* *ibid.*, page 28.

TABLE IX.—TENSILE PROPERTIES OF ZIRCONIUM-MOLYBDENUM ALLOYS.*

Composition			Testing temperature °C.	Yield strength 0.2% offset p.s.i.	Ultimate strength p.s.i.	Elongation %	Reduction in area %	Rockwell hardness B
Mo %	C %	Fe %						
0-1	0-17	0-16	Room	71,500	100,400	17	41-4	98
0-9	0-21	0-07		82,000	113,000	15	31-5	100
2-3	0-38	0-03		84,800	127,000	1	0-79	106
2-9	0-25	0-14		—	129,700	2	0	114
2-3	0-31	0-12		—	121,000	2	0	116
7-8	0-12	0-08		130,600	128,800	7-5	24-4	105
10-0	0-13	0-04		136,300	145,000	7-0	12-8	104
0-9	0-21	0-07	650	12,060	20,910	38-0	66-0	—
2-3	0-38	0-03		11,330	25,550	27-0	38-0	—
2-9	0-25	0-14		11,870	30,780	54-0	84-0	—
2-3	0-31	0-12		11,290	34,430	69-0	77-0	—
7-8	0-12	0-08		14,750	43,180	44-0	18-5	—
10-0	0-13	0-04		—	—	—	—	—

* *ibid.*, page 32.

TABLE X.—TENSILE PROPERTIES OF ZIRCONIUM-TITANIUM ALLOYS.*

Titanium content %	Yield† strength p.s.i. × 1,000	Ultimate strength p.s.i. × 1,000	Elongation % in 2 in.	Condition
3-2	42-5	85-4	17-3	Annealed 700° C.
3-2	83-5	134-6	7-2	As rolled 400° C.
15-0	74-2	90-8	1-5	Annealed 725° C.
35-0	110-0	138-8	2-7	Annealed 725° C.
35-0	97-6	148-4	5-0	20% cold reduced
50-0	113-2	140-4	1-5	Annealed 725° C.
50-0	89-4	152-4	1-0	20% cold reduced
65-0	115-0	125-9	1-2	Annealed 725° C.
65-0	114-6	128-9	0-5	20% cold reduced
85-0	78-0	101-4	1-0	Air cooled 900° C.

† At 0-05% offset.

* Article entitled "Ten Zirconium Alloys Evaluated" by F. B. Litton, *The Iron Age*, April 5th and 12th, 1951.

TABLE XI.—TENSILE PROPERTIES OF ZIRCONIUM-TUNGSTEN ALLOYS.*

Tungsten content %	Yield† strength p.s.i. × 1,000	Ultimate strength p.s.i. × 1,000	Elongation % in 2 in.	Condition
0-5	23-9	58-0	18-0	Annealed at 700° C.
0-5	32-6	67-7	17-3	Annealed at 700° C.
0-5	89-5	127-4	5-3	As rolled 400° C.
1-0	82-1	110-2	7-3	As rolled 825° C.

† At 0-05% offset.

* *ibid.*

The investigation of the zirconium-iron system by the Bureau was made the subject of a more intensive study than the other alloy systems because iron is usually present in varying amounts in zirconium, and it was

TABLE XII.—OXIDATION RESISTANCE OF Zr ALLOYS.*

Intended composition	Weight gain, Mg. per sq. dm.	
	Induction melt† 6 hr. at 750° C.	Arc melt 2 hr. at 750° C.
100% Zr	3,300	415
5% Ti, 95% Zr	Disintegrated	—
1% Al, 99% Zr	Disintegrated	—
4% Al, 96% Zr	—	550
5% Al, 95% Zr	—	413
5% Ta, 95% Zr	—	1,450
5% Nb, 95% Zr	Disintegrated	—
5% W, 95% Zr	—	2,600
5% Mo, 95% Zr	Disintegrated	209
5% Ni, 95% Zr	—	957
7-5% Ni, 92-5% Zr	—	1,690
5% Cr, 95% Zr	—	3,120
5% V, 95% Zr	—	3,198
5% Fe, 95% Zr	Disintegrated	—
5% Be, 95% Zr	Disintegrated	1,660
5% Si, 95% Zr	Disintegrated	—
50% Ti, 50% Zr	Disintegrated (a)	—
1% Al, 50% Ti, 49% Zr	Disintegrated (b)	Disintegrated (b)

(a) Alloy disintegrated in about 45 mins.

(b) Alloy disintegrated in about 19 mins.

* *ibid.*

† Graphite crucibles.

TABLE XIII.—OXIDATION RESISTANCE OF O₂-Zr AND N₂-Zr ALLOYS IN STILL AIR AT 750° C. FOR TWO HOURS.*

Oxygen Series		Nitrogen Series	
Oxygen content %	Weight gain mg. per sq. dm.	Nitrogen content %	Weight gain mg. per sq. dm.
0-041	153	0-013	600
0-044	129	0-061	313
0-059	150	0-079	227
0-073	121	0-080	474
0-105	131	0-091	1575
0-445	145	0-093	252
1-002	127	0-136	484
		0-144	318
		0-156	313
		0-408	248
Average	136-3	Average	480-4

* *ibid.*

TABLE XIV.—OXIDATION OF Zr CONTAINING Al, Ta, AND Nb IN AN AUTOCLAVE AT 315° C.*

Aluminum Series		Tantalum Series		Columbium Series	
Al content %	Weight gain, (a) mg per sq. dm.	Ta content %	Weight gain, mg per sq. dm.	Cb content %	Weight gain, (a) mg per sq. dm.
Zr base	14-6	—	—	—	—
0-05 Al-Zr	203-5	0-25 Ta-Zr	16-3 (b)	0-5 Cb-Zr	9-5
0-10 Al-Zr	394-0	1-5 Ta-Zr	wt. loss (a)	1-5 Cb-Zr	9-2
0-20 Al-Zr	696-0	7-0 Ta-Zr	51-1 (b)	30-0 Cb-Zr	72-6
0-30 Al-Zr	severely attacked	—	—	—	—

(a) 1 week test period; (b) 2 week test period.

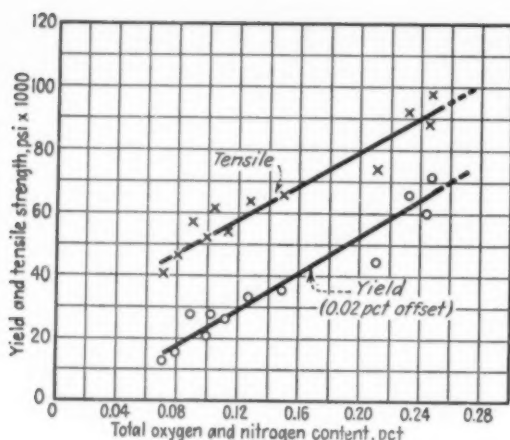
* *ibid.*

necessary to determine the effect on the physical and heat resisting properties. Actually, the addition of iron improved both properties considerably. The tensile properties of hot swaged rods of iron alloys containing up to 5-16% iron are shown in Table VIII.

In determining the heat resistance of the iron alloys it was found that increasing iron content reduced the corrosion rate rapidly although even the best were poor compared with 18-8 stainless steel.

Zirconium-molybdenum alloys containing up to 10% molybdenum were prepared and although their heat resistance was poor the additions had a marked effect on the tensile properties as shown in Table IX.

Metallurgists at the Foote Mineral Co. have studied a number of zirconium alloy systems for the U.S. Air



Courtesy of The Iron Age

Fig. 1.—The effect of oxygen and nitrogen combined on the tensile and yield strengths of samples annealed at 700° C.

Material Command. They report that the alloys investigated show reduced oxidation resistance but offer improved mechanical properties. Four methods of alloy preparation were examined. Melting in graphite was first tried, as it appears to be more readily adopted for commercial use, but it was discarded when it became apparent that the carbon contamination seriously reduced the oxidation resistance of the alloys.

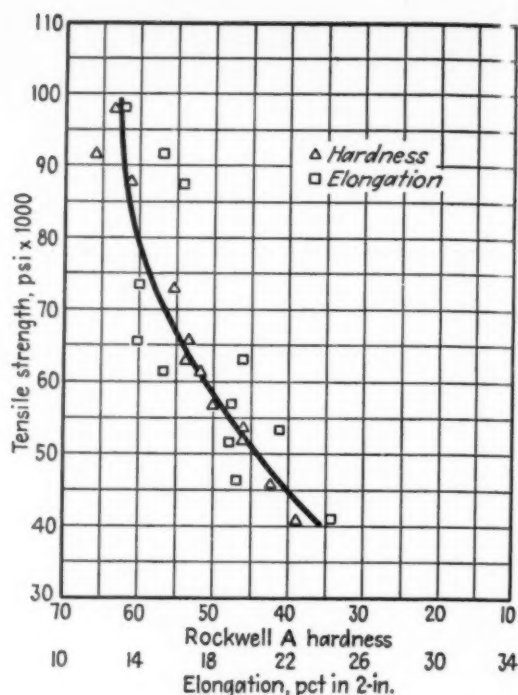
Carbon contamination was avoided by the use of an arc furnace consisting of a water-cooled copper crucible and movable tungsten electrode. The melts were prepared in an atmosphere of purified argon.

A rather unusual method of preparing the alloys was examined. This was a modification of the van Arkel or Iodide process and the alloys were obtained by co-deposition of the metal from the vapour of the mixed iodides. Diffusion of metals into zirconium was also used as a method of preparing some of the alloys.

The alloying elements investigated were hafnium, titanium, aluminium, tantalum, columbium, tungsten, copper, molybdenum, oxygen and nitrogen. The most interesting alloys are hafnium, oxygen and nitrogen because hafnium is present in all commercial zirconium as the cost of removing it from the mineral would be excessive. Oxygen and nitrogen are also present in the metal in variable quantities depending on the care taken during processing to exclude air.

Hafnium additions from 0.10-8.2% were made by using minerals with varying hafnium contents and zirconia chemically treated to decrease or increase the hafnium content. Iodide bars were produced and heat treated in zirconium cans at temperatures from 700°-925° C. before testing (some bars were arc melted). The results indicated that the tensile and yield strengths, allowing for experimental errors, showed no change due to the hafnium.

Titanium additions at 50% showed the maximum tensile and yield strengths (Table X). Additions of aluminium up to 4% decreased workability but improved strength. Tantalum alloys up to 27% were workable at 900° C. and the maximum strength was obtained at about 17.5% tantalum. Columbium was not as satisfactory as tantalum, the alloys being less workable.



Courtesy of The Iron Age

Fig. 2.—Tensile strength/hardness relationships on the oxygen plus nitrogen alloys plotted in Fig. 1.

Small additions of tungsten up to 1% induced considerable improvement in mechanical strength and were equivalent in their effect to much larger quantities of titanium and aluminium (Table XI).

Molybdenum alloys gave similar results to the tungsten series while copper additions up to 2.9% had little effect.

The effect of oxygen and nitrogen on the mechanical properties are shown in Figs. 1 and 2. The composition was varied by additions of up to 0.3% oxygen and 0.15% nitrogen. The actual content was determined after rolling at 400° C. in air. The samples were annealed at 700° C. before testing and the figures show that the yield and tensile strengths increased with rising oxygen and nitrogen contents, and in addition, good elongation values were obtained.

The ratio of tensile to yield strength varied from 0.32-0.73 and increased with the oxygen and nitrogen additions. It is interesting to note that at 0.058% oxygen and 0.013% nitrogen, which are typical figures for Iodide metal, the ratio was 0.32 while at 0.102% oxygen and 0.145% nitrogen, the approximate composition limit for ingot reduction at 400° C., the ratio increased to 0.73. The maximum addition of oxygen and nitrogen was 0.102% oxygen and 0.145% nitrogen, and this produced the highest strength alloy at 71,600 p.s.i. yield and 97,800 p.s.i. tensile strength. The elongation for this alloy was 13.1% compared with about 23.5% for the alloy with the lowest oxygen and nitrogen content (combined oxygen and nitrogen content 0.07%). The hardness figure for the stronger alloy was about 63 Rockwell A compared with about 38 for the alloy with the least content of oxygen and nitrogen.

Continued on page 220

Theory of Hollow Sinking of Thin-Walled Tubes

By S. Y. Chung, Ph.D., B.Sc., (Eng.) (Hons.), A.M.I.Mech.E., A.M.I.Prod.E.

Plug drawing is virtually a combination of hollow sinking and wall ironing operations so that stress and strain analysis for hollow sinking will hold good for plug drawing up to the point where ironing starts. Using a modified criterion of plastic yielding, the author discusses the theoretical aspects of hollow sinking and compares his theoretical stresses with previously published experimental results on highly pre-strained phosphorus-deoxidised copper and soft brass, and his predicted strains with recent research data on aluminium and brass.

IN the manufacture of both seamless and welded tubes, especially the former, the cold drawing process occupies an important place in the plant. The main objects of cold drawing are (1) to reduce the tube diameter, (2) to attain finer tolerance, (3) to improve the mechanical properties of the tube material, and (4) to increase the degree of surface finish.

In commercial practice, there are two general modes of cold drawing of tubes; one is hollow sinking and the other plug drawing. In the former, the tube is drawn through the die freely, as shown in Fig. 1a, whereas in the latter a restrictive plug or mandrel is inserted inside the tube to control the final wall thickness as well as the outside diameter, as indicated in Fig. 1b. Careful examination of these two methods of cold drawing shows that plug drawing is virtually the combination of both hollow sinking and wall ironing operations, and hence the stresses and strains analysis for hollow sinking will hold good for plug drawing up to the point where ironing starts. Although a few mathematical analyses have been published, some neglect the thickness variation during the drawing process and others assume an idealised stress-strain relationship.

Modified Criterion of Plastic Yielding

Various criteria have been suggested for defining the condition of plastic yielding since the latter part of the nineteenth century. The relations between these theories may best be visualised by representing the shape of the limiting surface of yielding $F(p_1, p_2, p_3) = 0$ in a right-angled co-ordinate system with axes p_1, p_2 and p_3 . In this way, the maximum stress theory is represented by a cube, the maximum strain theory by an oblique parallelepiped, the maximum shear stress theory by a hexagonal prism, the shear resilience theory by a cylinder, and so on.

Of these hypotheses regarding the stress conditions for plastic yielding, only the shear resilience criterion (von Mises's hypothesis) and the maximum shear-stress criterion (Tresca's hypothesis) are widely used at the present time. When the stress conditions are such that $p_1 > 0 > p_2$, and $p_3 = 0$, the von Mises criterion gives the plasticity condition as

$$p_1^2 - p_1 p_2 + p_2^2 = f^2 \quad (1)$$

where f is the yield stress in uni-axial tension. Under the same stress condition, Tresca's criterion, however, stipulates that plastic yielding will occur when

$$p_1 - p_2 = f \quad (2)$$

These two criteria are shown graphically in Fig. 2 over

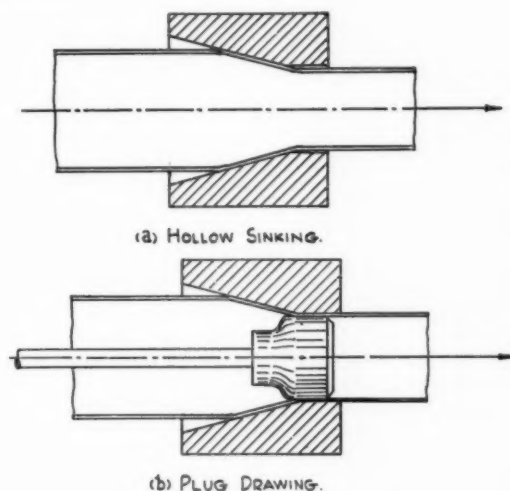


Fig. 1.—Method of cold drawing tubes.

their valid range. For non-ferrous metals, such as aluminium, brass and copper, it has been proved experimentally by various investigators that von Mises's criterion gives better results than Tresca's. On the other hand, Tresca's criterion is mathematically simpler by reason of its linear relationship instead of von Mises's second-order expression. As a compromise between the advantages and disadvantages of these two hypotheses, the following modified criterion of plastic yielding has been proposed, namely,

$$p_1 - p_2 = j.f \quad (3)$$

in which j is the best constant obtained by the method of Least Squares to satisfy von Mises's criterion, and is found to be 1.10. The graphical representation of this modified criterion is also shown in Fig. 2 in comparison with both Tresca's and von Mises's hypotheses.

Theoretical Treatment

This treatment is based on the assumption that (a) despite the presence of the frictional force at the interface of the metal and die, the normal pressure remains as one of the principal stresses, and (b) the wall thickness of the tube is small in comparison with the diameter of the tube so that bending effects may be neglected, and the stress distribution can be regarded as uniform across the cross-section of the wall.

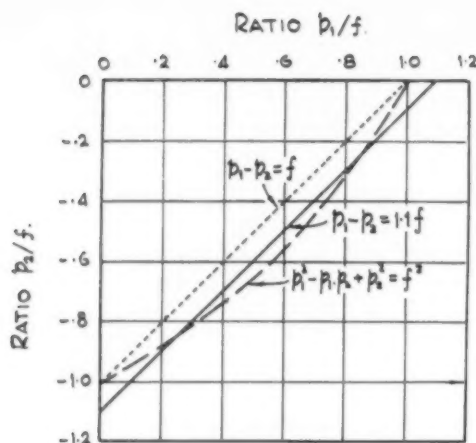


Fig. 2.—Graphical representation of yielding criteria.

Consider an elementary ring of metal in the tube which is in contact with the die. The principal stresses for this elementary ring are those shown in Fig. 3, in which p_r is defined as the radial stress, p_t as the lateral or thickness stress, and p_c as the circumferential stress.

With the notations given in the same figure,* the summation of the horizontal forces acting on half the elementary ring gives

$$2p_c t \cdot \delta s - p_r \cdot \delta s \cdot 2r \cdot \cos \theta + \mu \cdot p_t \cdot \delta s \cdot 2r \cdot \sin \theta + p_r t \cdot 2r \cdot \sin \theta - (p_r + \delta p_r)(t + \delta t) 2(r + \delta r) \cdot \sin \theta = 0$$

After simplifying, this becomes

$$p_c t \cdot \delta s - p_r \cdot \delta s \cdot r \cdot \cos \theta (1 - \mu \tan \theta) - \sin \theta \cdot d(p_r t \cdot r) = 0 \quad (4)$$

The summation of all the vertical forces on the whole ring yields

$$2\pi r \cdot p_t \cdot \delta s \cdot \sin \theta + \mu \cdot p_r \cdot \delta s \cdot 2\pi r \cdot \cos \theta + p_c \cdot 2\pi r t \cdot \cos \theta - (p_r + \delta p_r)(t + \delta t) 2\pi(r + \delta r) \cdot \cos \theta = 0$$

which reduces to

$$p_r \cdot \delta s \cdot r \cdot \sin \theta (1 + \mu \cot \theta) - \cos \theta \cdot d(p_r t \cdot r) = 0 \quad (5)$$

Eliminating p_t between equations (4) and (5), and putting $\delta s = \delta r / \sin \theta$ we have

$$p_c t \cdot (1 + \mu \cot \theta) - \frac{d}{dr}(p_r t \cdot r) = 0 \quad (6)$$

Substituting the modified criterion of plastic yielding and then re-arranging, equation (6) becomes

$$dp_r = -1.1(1+m) \cdot f \cdot \frac{dr}{r} + p_r \left(m \frac{dr}{r} - \frac{dt}{t} \right) \quad (7)$$

in which $m = \mu \cot \theta$.

When the effect of thickness variation is neglected, as in the paper by Sachs and Baldwin¹ (1946), the differential equation for the evaluation of the principal radial stress becomes

$$dp_r = -1.1(1+m) \cdot f \cdot \frac{dr}{r} + p_r \cdot m \cdot \frac{dr}{r}$$

and when the effect of die friction is further neglected, the radial stress becomes simply

$$p_r = -1.1 \int f \cdot \frac{dr}{r}$$

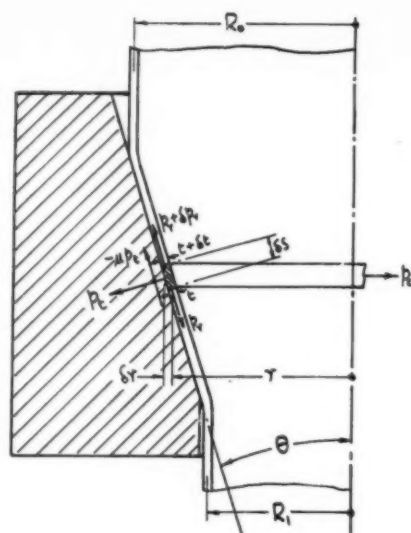


Fig. 3.—Stresses acting on an elementary ring.

In order to take the effect of thickness changes into account in the present analysis, we have to introduce the Levy-Mises stress and strain-increment relations,

$$\frac{dt}{t} = \left[\frac{2p_t - p_r - p_c}{2p_c - p_t - p_r} \right] \frac{dr}{r}$$

Of the three principal stresses in hollow sinking of thin-walled tubes, p_t is always relatively small,

$$p_t = \frac{t}{r} p_c \cos \theta$$

and for all ordinary purposes may be neglected.

Hence we may write

$$\frac{dt}{t} = \left[\frac{p_r + p_c}{p_r - 2p_c} \right] \frac{dr}{r} \quad (8)$$

Putting $p_r = p_c = 1.1f$, and re-arranging, equation (8) becomes

$$\frac{dt}{t} = - \left[2 + \frac{3 \cdot 3 f}{p_r - 2 \cdot 2 f} \right] \frac{dr}{r} \quad (9)$$

Substituting equation (9) into equation (7), we have

$$dp_r = -1.1(1+m) \cdot f \cdot \frac{dr}{r} + p_r \left[m + 2 + \frac{3 \cdot 3 f}{p_r - 2 \cdot 2 f} \right] \frac{dr}{r} \quad (10)$$

In a recent paper by H. W. Swift² (1949), it was assumed, for analytical reasons, that the yield stress f takes the form $f = f_0 + c \cdot p_r$, in which c is a measure of the constant strain-hardening rate with respect to the radial stress p_r .

In the present analysis, it is proposed to represent the stress-strain characteristic of the material by the more appropriate Ludwik's power law of the form

$$f = f_0 + B \cdot \ln^n \left(\frac{R_0}{r} \right)$$

in which f_0 , B , and n are constants.* It is found that

2 H. W. Swift. *Philosophical Magazine*, 1949. **XL**, 883.

* For analytical convenience and consistency, these normal stresses will be regarded as positive when tensile.

1 Sachs and Baldwin. *Trans. A.S.M.E.* 1946. **68**, 655.

It is assumed here that the Effective Strain $(\bar{\epsilon} = \sqrt{\frac{2}{3}} \sqrt{de_1^2 + de_2^2 + de_3^2})$ is numerically equal to the circumferential strain during sinking; the error being about a few per cent. over the practical range of reduction. de_1 , de_2 and de_3 are respectively the three principal incremental strains.

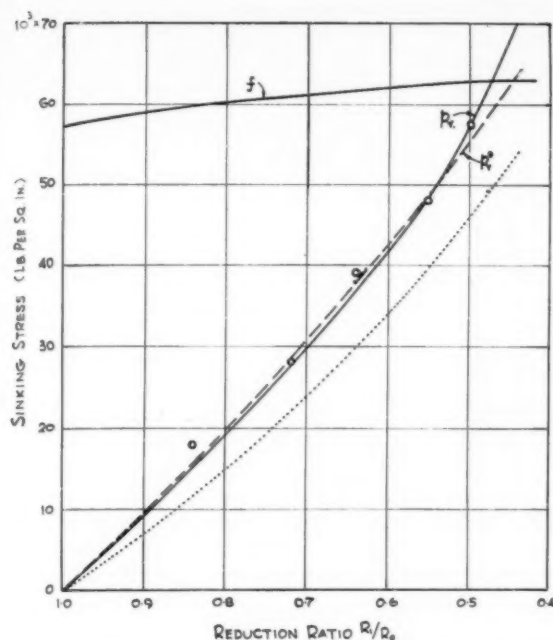


Fig. 4.—Theoretical and experimental sinking stress for hard copper.

this form will fit all possible stress-strain relationships of the common materials to a considerable degree of accuracy on one hand, and is mathematically simple enough for manipulation purposes on the other. The value of n varies from zero for a non-hardening material to a maximum value of unity for metals which have very marked strain-hardening properties.

The exact solution of the differential equation (10) is unwieldy, but fortunately the maximum value of the second term on the R.H.S. of the differential equation under ordinary conditions does not exceed about 10% of the first term. It is found that, for practical purposes, we may write, within an error of about 1%,

$$dp_r \approx -1.1(1+m)f \cdot \frac{dr}{r} + m \cdot p_r' \cdot \frac{dr}{r} + \left[2 + \frac{3.3f}{p_r' - 2.2f} \right] \cdot p_r' \cdot \frac{dr}{r} \quad (11)$$

$$\text{in which } p_r' = -1.1(1+m) \int f \cdot \frac{dr}{r} \quad (12)$$

$$\text{and } p_r'' = p_r' + m \int p_r' \cdot \frac{dr}{r} \quad (13)$$

where p_r' is the sinking stress required when the effect of the thickness changes is neglected.

Substituting $f = f_0 + B \cdot \ln(R_0/r)$ into equations (12) and (13), and integrating between appropriate limits, we have

$$p_r'' = 1.1(1+m)f_0 \left[1 - \frac{1}{2}m \cdot \ln \frac{R_0}{r} \right] \ln \frac{R_0}{r} + \frac{1.1(1+m)B}{(1+n)} \left[1 - \frac{m}{2+n} \cdot \ln \frac{R_0}{r} \right] \ln^{1+n} \left(\frac{R_0}{r} \right) \quad (14)$$

Thus the radial stress required to sink a given tube from initial mean radius R_0 to current mean radius r is

$$p_r = p_r'' + \int_{R_0}^r p_r' \cdot \left[2 + \frac{3.3f}{p_r' - 2.2f} \right] \frac{dr}{r} \quad (15)$$

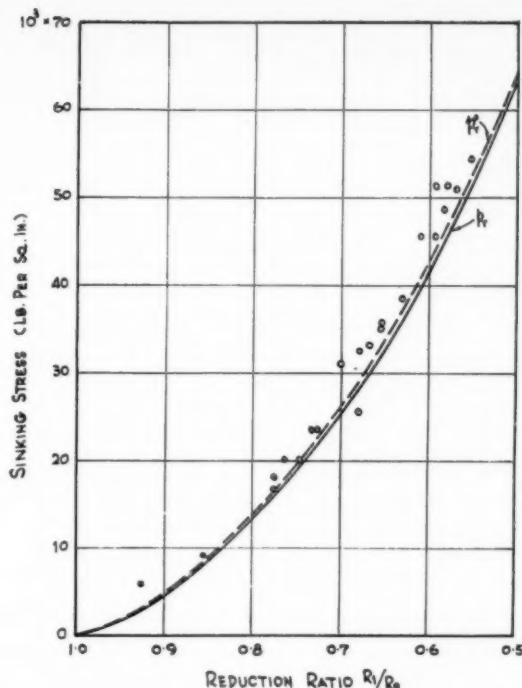


Fig. 5.—Theoretical and experimental sinking stress for soft brass.

the integration of which may be carried out numerically.

When the resultant sinking stress p_r is known, the principal logarithmic thickness strain, e_t , may be calculated by integrating equation (9), and the corresponding logarithmic axial strain e_a can be computed from the equation of constancy of volume. Accordingly, the development of the three principal strains during hollow sinking can be evaluated and plotted if desired. The corresponding unit or engineering strains e' , which are better known in practice, may be deduced from the relationship $e = \ln(1 + e')$.

Comparison between Theory and Experiment

(1) *Stresses*: For the comparison of the theoretical and experimental sinking stresses, some experimental results published by Sachs and Baldwin in 1946³ are reproduced in Figs. 4 and 5. In their experiments, the ratio t_0/R_0 is approximately 0.06 and a commercial soap-base lubricant was used throughout. In Fig. 4, the experimental results, which are represented by the hollow circles, were obtained by hollow sinking of a highly pre-strained phosphorus deoxidised copper having a very flat stress-strain relationship (as indicated in the same figure) in a 14° half-cone-angle die. It is seen that if we assume the yield stress is constant at $f = 60,000$ lb./sq. in. the average error in the value of f is of the order of about $\pm 3\%$. When both die friction and thickness changes are neglected, the theoretical sinking stress is represented by the dotted curve, which underestimates the actual sinking stress by as much as 20%. When friction is taken into consideration ($\mu = 0.1$), the theoretical sinking stress p_r'' is shown by the dashed curve, whereas the solid-line curve stands for the sinking

³ Sachs and Baldwin, *Op. cit.*

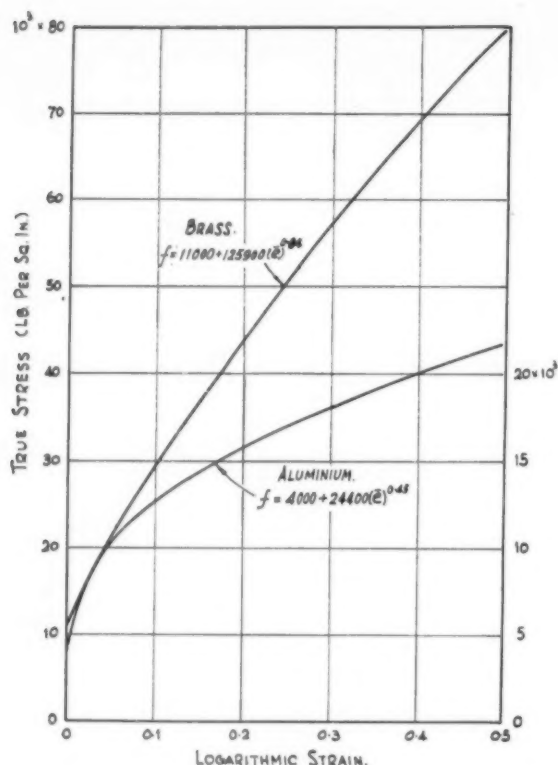


Fig. 6.—Stress-strain curves for aluminium and brass.

stress p , when both friction and thickness variation are taken into account. For reduction ratios not less than 0.54 the effect of thickness changes tends to lower the sinking stress very slightly, but it tends to raise it rapidly as the reduction ratio is less than 0.54.

The experimental results in Fig. 5, plotted as hollow circles again, were obtained by Sachs and Baldwin³ by sinking soft brass tubes under the same conditions as above. This particular material exhibits a very marked strain-hardening characteristic, and the stress-strain curve given by Sachs and Baldwin may be represented within $\pm 3\%$ by $f = 14,000 + 107,000(e)^{0.73}$. The dashed curve represents the theoretical sinking stress p_s^* with friction ($\mu = 0.175$) but neglecting the thickness changes, whereas the solid-line curve gives the corresponding sinking stress p , when both friction and thickness variation are taken into account. The effect of thickness variation in this case, where the material has a very high strain-hardening property, lowers the sinking stress slightly over the whole relevant range.

On the whole, the effect of thickness changes on the sinking stress is comparatively small (not more than 5%), and the simplicity achieved by its neglect is justifiable in industrial practice.

(2) *Strains*: The comparisons of the theoretical and experimental development of the principal strains are made on both aluminium and brass tubes of initial outside diameter $\frac{1}{2}$ in. and initial thickness $\frac{1}{8}$ in.* The sinking was carried out in the 15° half-cone-angle die, which was lubricated with graphite in tallow (1:3

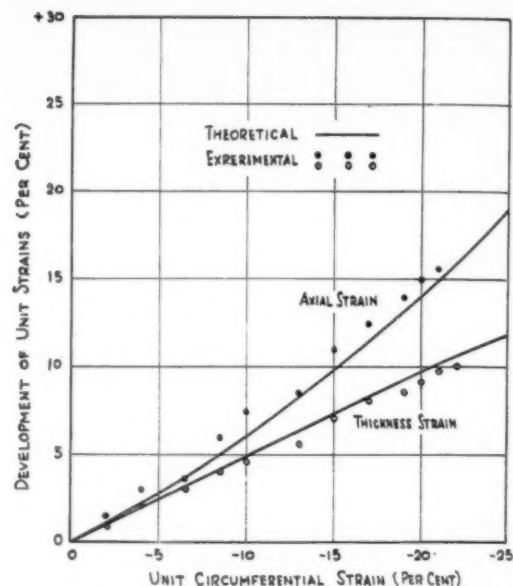


Fig. 7.—Theoretical and experimental development of strains for brass.

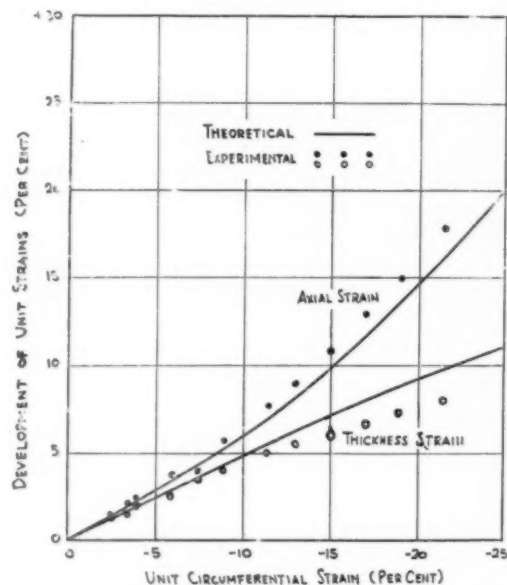


Fig. 8.—Theoretical and experimental development of strains for aluminium.

mixture by weight). The stress-strain curves for these two materials are shown in Fig. 6, and these are obtained by the ordinary standard tensile tests made on specimens cut longitudinally from the tubes.

The strain comparisons for brass and aluminium are shown graphically in Figs. 7 and 8 respectively. The theoretical values are represented by the solid-line curves, whilst the experimental results are represented by the hollow circles for the thickness strain and by the solid circles for the axial strain. In these theoretical calculations, a coefficient of friction of 0.1 was used. It is seen that the correlation between theory and experiment is reasonably good.

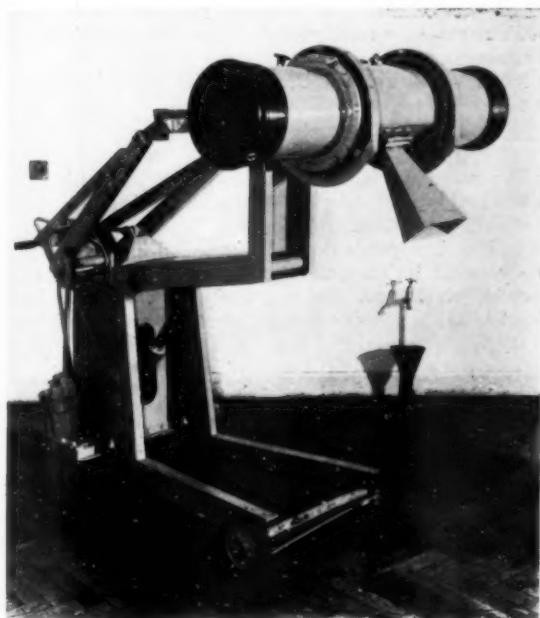
* The author wishes to thank Professor H. W. Swift of Sheffield University for permission to use the experimental results obtained in his Engineering Research Laboratory by Mr. B. M. Botros, M. Eng.

RECENT DEVELOPMENTS

MATERIALS : PROCESSES : EQUIPMENT

A New Industrial X-Ray Unit

DURING the past two decades, much progress has been made in the design of X-ray equipment more in keeping with industrial problems. A recent example is the "Compactix" unit, which is entirely new in conception, and which the makers claim greatly simplifies procedure and leads to a speedier rate of inspection.



Cylindrical in form the X-ray unit proper is subdivided internally by two insulating partitions. The high-voltage energising source comprises two specially designed transformers, each complete in itself and each developing 100 kVp to earth. Both transformers, together with the X-ray tube, are oil immersed, the tube being housed in the central compartment. The transformers are directly connected to the tube with which they are thus in series, an additional filament-heating transformer being provided on the cathode side. Continuously rated at 200 kVp 10 mA, the tube acts as its own rectifier and there are no valves or high tension cables. The X-ray beam emerges from a window in the wall of the container, the position of the focus being the geometric centre of the whole. Water cooling is applied to the anode of the tube and to the oil.

The control unit is of very small dimensions and designed to facilitate easy transport. Reproducible operating conditions are made possible by means of a mains compensator. A stepless auto-transformer, working in conjunction with a kilovoltmeter, enables the penetration to be controlled with a high degree of precision. The tube current, which can be varied, is indicated by a milli-ammeter. A protective circuit prevents the apparatus from being switched on or

alternatively it is switched off automatically if for any reason the water supply should be interrupted. Cooling is normally effected from the water main, but the makers also offer a trolley mounted closed circuit system for use in the field or where mains water supply is not reliable.

The illustration shows the "Compactix" unit mounted on a truck with hydraulically operated raising and lowering gear, permitting a very wide range of vertical adjustment. For use in shipyards and on out-door structures, the X-ray head is provided with slings so that it can be used quite independently of any other form of mounting. For such work the cylindrical form of the tube head permits of easy passage through a manhole. The equipment is completely shockproof and suitably X-ray protected, and its operation is unaffected by humidity or altitude.

The "Compactix" unit, it is stated, has a radiographic penetration of 3 in. of steel in an economical exposure time, and is constructed to operate from a single phase supply 220/250 volts 50/60 cycles.

Philips Electrical, Ltd., Century House, Shaftesbury Avenue, London, W.C.2.

Cold Junction Thermostat

WITH the increasing demands for maximum efficiency in temperature measurement, cold junction temperature control becomes a factor of major importance. If vacuum flasks are used there is the difficulty of ice



supply, and the nuisance of having to add more ice from time to time, whilst oil-filled vacuum flasks are subject to slow temperature changes which must be allowed for in final calculations. Stirring of the ice or liquid is also necessary to prevent stratification. Where a bi-metallic temperature compensator is incorporated in the indicator, expensive compensating cable is required.

The Sunvic Cold Junction Thermostat is designed to overcome these difficulties and consists of a solid aluminium body, wound with a small heater and enclosed in a bakelite cylinder. The aluminium cylinder is drilled to house the thermocouples and thermometer and the heater is controlled by a proportional thermostat giving control to within 0.1°C. The instrument is supplied set to a temperature between 42°C. and 48°C. Under normal conditions, the instrument will stabilise approximately 45 minutes after switching on, after which it will maintain its temperature despite changes in ambient temperature or mains voltage.

Sunvic Controls, Ltd., Sunvic House, 10, Essex St., London, W.C.2.

New Refractory Products

SHOWN for the first time at the recent British Industries

Fair were two new products of The Morgan Crucible Co., Ltd. The first was the Morgan M.R. Refractory, which constitutes an outstanding and most valuable contribution to industrial productivity. It is a super-duty refractory manufactured to a standard never previously approached in the British Commonwealth. The use of selected raw materials and a specialised method of manufacture have resulted in producing the following characteristics: (a) volume stability at high working temperatures; (b) remarkable resistance to thermal shock; (c) unusually high resistance to slag attack.

The other item was the most recent addition to the Salamander crucible range, the Salamander Suprex, specially suited for extremely arduous conditions and where particularly erosive fluxes must be used. They will also meet the full demands of the latest rapid heating techniques.

The Morgan Crucible Co., Ltd., London, S.W.11.

British Standards Institution New and Revised Standards

METHODS FOR THE ANALYSIS OF IRON AND STEEL
(B.S. 1121: 1951, Pts. 19, 20, 21)

PART 19 deals with the absorptiometric determination of up to 0.05% silicon using the molybdenum blue colour developed from the reduction of silico-molybdate.

Part 20, for the determination of tin, is based on the isolation of tin as the sulphide, using molybdenum sulphide as a carrier agent, solution and reduction of the tin to the bivalent condition with metallic aluminium in the presence of an antimony salt and normal titration of the reduced tin with standard iodate.

Part 21 for the determination of aluminium oxide is based on the separation of insoluble aluminium oxide when the sample is treated with a mixture of methyl alcohol and bromine. The residue is fused with potassium bisulphate, extracted in dilute sulphuric acid, and iron and titanium are separated by precipitation with cupferron. Aluminium is precipitated with 8-hydroxyquinoline and the compound is either weighed or titrated.

COLOUR IDENTIFICATION OF PIPE LINES
(B.S. 1710: 1951)

OF recent years considerable attention has been given to the use of colour for the identification of pipe lines and a number of difficulties have arisen because of differing opinions as to whether the identification should be on the basis of the characteristics of the pipe content or the identification of the pipe content as such. During the past twenty years three British Standards have been published dealing with the identification of piping, and certain anomalies have arisen. In order to remove these difficulties, and to co-ordinate requirements, this code has been prepared and replaces B.S.457—'Identification of chemical pipe lines,' B.S.617—'Identification of pipes, conduits, ducts and cables in buildings,' and B.S.3011—'Identification colours for engine room piping,' but it does not supersede the British Standards dealing with gas cylinders and medical gas cylinders nor does it affect the provisions of B.S.158, which deals with the colour identification of switchgear bus-bars and connections and wire.

The standard itself provides primary identification colours which indicate the class of content in pipe lines, these colours being applied along the length of the pipe or in broad rings, as desired. Detailed identification of the content by narrow rings or letters and for certain special conditions are covered in the appendices. Consideration has shown that, since only a limited range of colours is suitable for use under all conditions without confusion being caused through fading or discoloration, any highly complex scheme for identification is unlikely to be really practicable and a simple code has been evolved. Coloured illustrations of the application of the code are included.

Copies of the above Standards may be obtained from the British Standards Institution, Sales Department, 24, Victoria Street, London, S.W.1. The post-free prices are as follows: B.S. 1121, Parts 19, 20, 21, 1s. each; B.S. 1710, 2s. 6d.

Zirconium-Production, Properties and Alloys

(Continued from page 214)

In general, the oxidation resistance of zirconium is not improved by alloying although, to some extent, minor additions of aluminium and nitrogen reduced oxidation resistance, while oxygen slightly increased. The results of tests carried out by the Foote Mineral Co. are shown in Tables XII, XIII and XIV.

BIBLIOGRAPHY

- 1 "Production of Malleable Zirconium on a Pilot Plant Scale," W. J. Kroll, W. W. Stephens and H. P. Holmes, *Journal of Metals*, **188**, 1950, 1445-1453.
- 2 "Improvements in Methods for the Reduction of Zirconium Chloride with Magnesium," W. J. Kroll, W. F. Hergert and L. A. Yerkes, *Journal of Electrochemical Society*, **97**, (10), 1950, 305-310.
- 3 "Continuous Method of Producing Ductile Zirconium," P. J. Madden and L. W. Eastwood, *Journal of Metals*, **188**, (4), 1950, 634-640.
- 4 "Production of Titanium from Titanium Tetrachloride in an Arc Furnace," L. D. Jaffe and R. K. Pitler, *Journal of Metals*, **188**, (11), 1950, 1396.
- 5 "Attempts to Electrodeposit Zirconium," M. L. Holt, *Journal of Electrochemical Society*, **98**, (3), 1951, 333.
- 6 "Electrodeposition of Zirconium," Japanese Patent 172,621.
- 7 "Preliminary Survey of Zirconium Alloys," C. T. Anderson, E. T. Hayes, A. H. Roberson and W. J. Kroll, Bureau of Mines Report No. 4658, March, 1950.
- 8 "Constitution and Mechanical Properties of Zirconium-Iron Alloys," E. T. Hayes, A. H. Roberson, and W. C. O'Brien, *Trans. American Society for Metals*, Preprint No. 29.
- 9 "Ten Zirconium Alloys Evaluated," F. B. Kitton, *Iron Age*, April 5th and 12th, 1951.

Recent Heat Treatment Installations

Exacting Demands of Modern Engineering Govern Design

As the demand for materials having improved properties increases, so does the need for accurate and reliable heat treatment. This, in turn, calls for heat treatment plant that is reliable, simple to operate, and conducive to good working conditions. Designers of such equipment are constantly effecting improvements, and some recent installations, incorporating the latest developments, are briefly described in this article.

DEMAND for heat treatment plant has continued during the past 12 months and considerable progress has been made in the development of equipment incorporating the most recent advances in heating and mechanical handling. The effect of these has been increased production, more consistent treatment, and less time spent on subsequent finishing. So many improvements have been incorporated in recent installations that it is only possible to refer to some of them as typical examples; to simplify their presentation the furnaces, as far as possible, will be divided into groups according to purpose.

Reheating Furnaces

The need for uniformity in the reheating of material for shaping into various forms has long been recognised, and modern furnaces now have fully automatic control; in addition, however, particular attention has been given to the mechanical handling of the material with a view to high production and a reduced operating staff. A typical installation of this kind is the plant for reheating copper bars prior to rolling at the works of Enfield Rolling Mills, Ltd. This plant was designed and constructed by The Wellman Smith Owen Engineering Corporation, Ltd., and comprises a continuous-type reheating furnace with fully automatic control, two 5-ton transfer cars, an electric overhead travelling

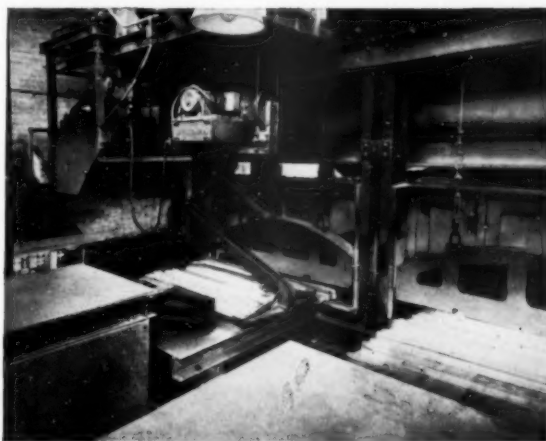


Fig. 2.—Showing the electric overhead travelling Telfer transferring a row of copper bars to the charging platform.

Telfer with a capacity of 35 cwt., and two rack and pinion type single ram pushers.

The furnace has two chambers each 36 ft. long by 6 ft. wide. Near the discharge end there are top and bottom heating zones. Each heating zone is constructed of a Carbofrax muffle arch having a span of 6 ft. to ensure correct and uniform heating of the copper bars. Each bottom heating zone comprises three chambers having Carbofrax muffle arches causing even heating of the bars, making due allowance for the water-cooled skids. As will be noted in Fig. 1, the heated bars are discharged from the furnace via a sloping ramp, the bars being then conveyed by means of a live roller table to the rod mill.

The furnace is fired by heavy fuel oil and consumes 4.5 galls. per ton when heating 27 tons per hour of bars from cold to 850° C.; the oil is pumped to the burners at a pressure of 25 lb./sq. in. Babcock & Wilcox oil burners are used, eight in the upper heating zones and six in the lower ones. The products of combustion are exhausted from the furnace through equally distributed ports in the hearth, near to the charging door, and are conveyed through an underground flue to a metallic needle type recuperator which preheats the combustion air to 300° C. Automatic control is effected by Reavell Askania instruments and, in addition to temperature and pressure control, correct oil/air ratio is assured. The instruments incorporate Lockheed hydraulic hand control gear.

An interesting reheating furnace development has been described recently in a report issued by The Gas

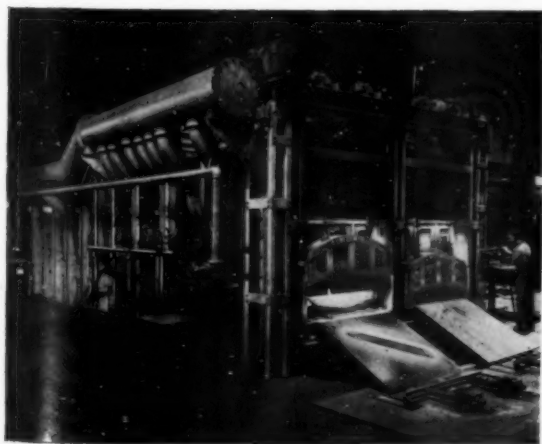


Fig. 1.—Continuous furnace for reheating copper bars prior to rolling. Fired by heavy fuel oil, the furnace has two chambers, each 36 ft. long and 6 ft. wide. It was designed and constructed by The Wellman Smith Owen Engineering Corporation, Ltd., and is installed at the works of Enfield Rolling Mills, Ltd. The illustration shows the discharging end.

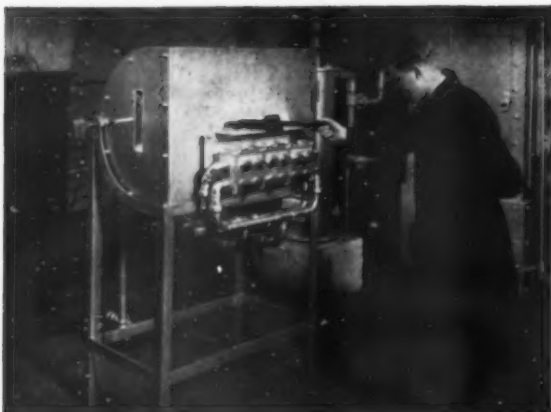


Fig. 3.—An automatically controlled slot forge furnace by the Thermic Equipment and Engineering Co., Ltd.

Council. It concerns an automatically controlled slot forge furnace (Fig. 3) made by the Thermic Equipment and Engineering Co. Ltd. In the past, the small slot forge furnaces in use in the cutlery and small-tool trades have been fired by opposed air-blast burners, the products of combustion being blown out at the working slot. This has resulted in inefficient, uneconomical and uncomfortable working and the new furnace has, therefore, been designed on reverberatory principles. The burners, situated below the slot, fire horizontally into the furnace, impinging on a curved surface lined with $\frac{1}{2}$ in. carborundum cement. This imparts a swirling motion to the hot gases which pass with relatively high velocity over, or through, any work placed in the slots. The flues are located at the ends of the furnace and have an oblique section from the working chamber to minimise

radiation loss. Hand control of the furnace is effected by two quadrant cocks, and provision is made for running at lower temperatures at meal times and slack periods. For fully automatic control, a Sunvic energy regulator is used in conjunction with an "on-off" type solenoid valve.

Annealing Furnaces

The range and variety of annealing furnaces is very considerable, the design depending on the type of work for which they are intended. Modifications and improvements have been effected in a number of designs previously described. In the May, 1948, issue, for instance, a description was given of a new portable-cover furnace designed for annealing silicon steel sheets in packs. Modified versions have since been built for the annealing of castings and forged steel work rolls. An installation of this kind was recently completed by The Dowson & Mason Gas Plant Co. Ltd., consisting of four town's gas fired furnaces, each having hoods 14 ft. 6 in. long, 9 ft. wide and 5 ft. 3 in. high. Each furnace is loaded with a charge consisting of 26 tons of forged steel rolls which are given a long and complicated heat treatment cycle.

This design has obvious advantages for dealing with work of this kind: the installation costs are lower than for any other type of furnace; the sand seal surrounding the hood is at the base, thus the gases of combustion in the furnace are at a higher pressure than in most furnaces; and the charge can be placed directly on the base with no restriction and no danger of subsequent movement. It incorporates a refractory base having 24 vertical-firing luminous-flame burners arranged along the sides to give an almost continuous curtain of flame from end to end so that the charge receives very uniform radiation. The products of combustion descend slowly through the charge to waste gas outlet ducts in the base at the ends. Under the refractory hearth a number of



Fig. 4.—A portable cover furnace for annealing castings and forged steel work rolls recently completed by The Dowson & Mason Gas Plant Co. Ltd., for Wm. Beardmore & Co. Ltd.



Fig. 5.—Showing a design feature of a stress relieving furnace recently installed at the works of The Fairey Aviation Co. Ltd., by The Dowson and Mason Gas Plant Co. Ltd.

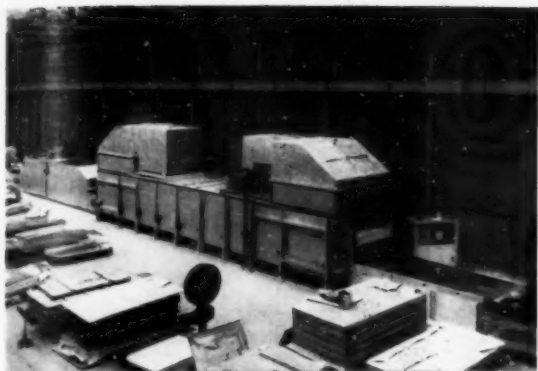


Fig. 6.—A continuous "flash" annealing furnace for aluminium sheets or circles. Designed and built by Stordy Engineering, Ltd., it will handle single sheets up to 5 ft. wide and circles down to 5 in. dia. at 1 ton/hour.



Fig. 7.—A pit type furnace by Stordy Engineering, Ltd., for the heat treatment of coiled light alloy tubes; it is designed to take a load up to 4 ft. 6 in. dia. by 8 ft. deep.

longitudinal ports are arranged through which the waste gases pass to a flue; this feature ensures that the bottom of the furnace is adequately heated.

Cold air from a low pressure fan enters a built-in manifold, from which it passes into individual recuperator elements consisting of two concentric metallic tubes. Air passes through the inner tube to the closed end of the outer tube where it changes direction, passing between the inner and outer tubes to the burner. When the air is preheated it does not again leave the interior of the furnace and so arrives at the burner at a high temperature. The gas manifold is also built in with integral gas control valves. The portable hood is lined with light insulating refractory material. Fig. 4 shows the hood being lowered on a base loaded with a charge.

A method of obtaining good uniformity at low temperatures, in a furnace designed for much higher temperature operation, is to equip it with additional secondary air-jets and mixing devices. In the higher temperature range, the furnace is operated in the normal manner with only the air for combustion passing through the burners. When uniform temperatures around 400°C . are required, additional air is admitted through an annulus in each burner block. This air is mixed with the gases of combustion in a refractory venturi in front of each burner. The temperature of the hot gas stream is greatly reduced and the volume increased, with the result that low temperatures can be obtained with uniform conditions throughout the working chamber. This is known as the "Ineraflo" air dilution system, and its practical effect is to give a normal furnace similar characteristics to the convection heated air recirculating type generally favoured for low temperature operation. Fig. 5 shows the system applied to a recently completed stress relieving furnace.

The usual process of "pack" annealing of aluminium alloy sheets and circles, in the more orthodox air-circulated batch furnaces, is rather a long one due to two limiting factors. The temperature "head" in the furnace must be limited to prevent overheating on the outer edges, and the packs, even when spacers are employed, do not lend themselves to thorough air circulation. Neither can any appreciable improvement be effected, because the temperature "head" cannot be widened. The continuous "flash" annealing of sheets does allow these two limiting factors to be adjusted and

the result is a product which has been heated to its annealing temperature in two or three minutes to give recrystallisation of the structure of the material, and elimination of rolling line, without allowing time for subsequent grain growth. A continuous plant for this purpose is shown in Fig. 6. Designed and built by Stordy Engineering, Ltd., it will handle single sheets up to 5 ft. wide and circles down to 5 in. dia. at the rate of 1 ton per hour. It consists of a loading conveyor interlaced with a furnace conveyor which is, in turn, interlaced with a cooling conveyor, which, finally, is interlaced with the unloading conveyor.

Air circulation is adopted for heating; two large volume centrifugal-type high temperature fans being disposed towards each end to supply air through the heater batteries into two sets of distributing ducts from which the air is directed on to the work. Further means are adopted to multiply the number of times the air is deflected over the work before it is returned to the fans and heaters. This method of two independent, balanced, air-circulating systems gives a true aerodynamic balance to the furnace. There are two heater batteries, one to each circulating system, and each battery is subdivided into lower ratings, but the total loadings of the batteries

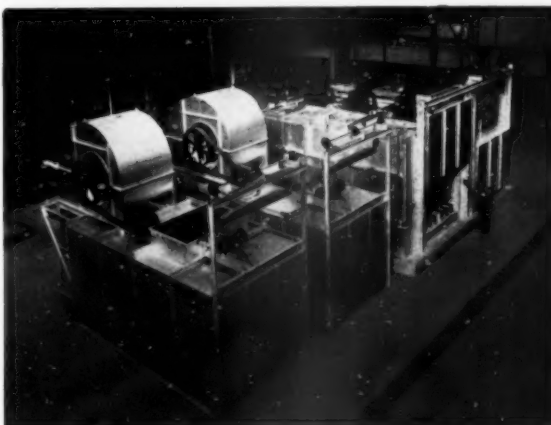


Fig. 8.—Double chamber coil annealing furnace, with capacity for 24 tons of aluminium alloy coils, by McDonald Furnaces, Ltd.



Fig. 9.—A general view of a continuous bright annealing furnace for steel strip recently installed at The Effingham Steel Works, Ltd., by The General Electric Co. Ltd. The furnace is about 120 ft. long and has a nominal output of 10 cwts. of strip per hour.

are unequal. Two control systems and contactor gear govern the operation of the furnace, and preselective switching of the various ratings is provided.

The annealing procedure is laid down for each thickness of sheet and circle as a function of furnace temperature and time, and the infinitely variable speed gear provided on the conveyor drive has been calibrated to read annealing times. The vital parts of this plant have been designed for easy maintenance and inspection, fan bearings are ring lubricated, water-cooled and thoroughly exposed, while the heating elements can be removed as a whole when necessary.

A similar principle is applied in the pit type furnace shown in Fig. 7, used for the heat treatment of coiled light alloy tubes. The heater battery is a unit construction and it is located outside the working chamber. It is also subdivided, thus permitting an optimum electrical loading being preselected for any production load; each sub-section is provided with its own contactor unit and the battery is controlled by a thermostatic control



Fig. 10.—A general view of the furnace shop at the Ambergate works of Richard Johnson & Nephew, Ltd., comprising three G.E.C. vertical cylindrical furnaces at the far end, with the recuperators next to them, and the cooling pits at the end nearest the camera.

system. The heat is conveyed to the working chamber by means of a large capacity centrifugal fan, the temperature head of the entering air being kept to a minimum. By means of the distributing and recirculating system, a highly turbulent condition is created throughout the working chamber, giving temperature control and uniformity of heating of the charge. The lid gear has received special attention and a sealing device ensures that the thermal system is completely closed when under operating conditions.

A new double-chambered coil-annealing furnace (Fig. 8), recently completed for the British Aluminium Co. Ltd., has a number of interesting features. Special consideration has been given to the distribution of the unusually high volume of circulating air developed from the motor-driven fans, which total 150 h.p. The heating elements, in the form of grid batteries, are accommodated in the roof and are supported on patent hooks for quick removal. Accessibility to each heater battery is important, and McDonald Furnaces, Ltd., have developed a simple construction of quick release panels



Fig. 11.—A 140 kW Birlec pit furnace for bright annealing coil strip at Samuel Fox & Co. Ltd. A new development is the fan motor and housing on top of the container.

which facilitates inspection. To obviate any delay when the charging machine operator is handling hot metal, up to 12 tons weight, the furnace door gears are designed to open and close in 5 seconds, without shock, thus eliminating any risk of damage to the furnace brickwork at the beginning and end of each stroke. Following annealing, each charge is delivered to a cooling chamber, which has a very large air capacity to ensure that cooling is completed within the corresponding heating time of the following charge.

For many years The Effingham Steel Works, Ltd., have used vertical cylindrical furnaces, made by The General Electric Co. Ltd., for the bright annealing of steel strip in coils. Now a new G.E.C. furnace has been installed for the continuous treatment of steel strip in lengths, in an atmosphere of partially burnt town's gas. The furnace, which operates on the roller hearth principle, is about 120 ft. in length, is rated at 22 kW, and has a nominal output of 10 cwts. of strip per hour. The strips to be normalised are placed side by side across the furnace, which has a loading width of 18 in. All thicknesses of material up to $\frac{1}{4}$ in. are treated, and the strips emerge at

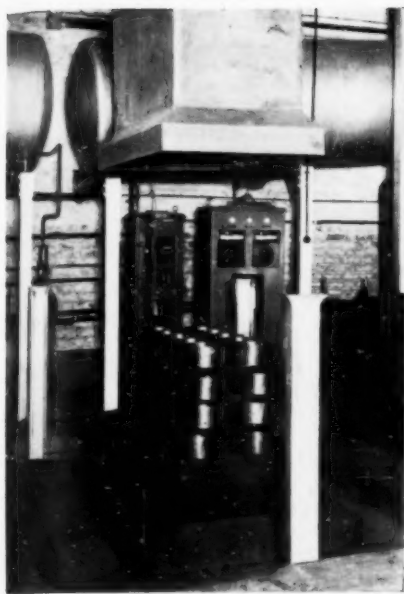


Fig. 12.—A rectangular bell-type furnace by G. W. B. Electric Furnaces, Ltd., for bright annealing cupro-nickel, copper, brass, nickel silver and other non-ferrous alloys.

the unloading end with surfaces unblemished by oxidation.

The furnace, a general view of which is shown in Fig. 9, is divided into several zones. The heating zone has three sections of equal length, each rated differently, the section with the highest rating being nearest the furnace entrance. The temperature of each section is independently and automatically controlled. Immediately before the first heating zone is a short section that is water-cooled to heat-insulate the ingoing end of the furnace from the heated chamber. Cooling the strip is carried out in two zones: a heat-insulated chamber designed to give slow cooling, and a water-cooled chamber of sufficient length to enable the charge to be handled on emerging from the discharge end. At both ends of the furnace is a combined atmosphere chamber and hood, with a flap to reduce atmosphere loss and also to prevent the entry of air. At the top of the hoods are short pipes fitted with gauze so that gas issuing from the ends of the furnace can be burnt.

An interesting installation for the bright annealing of wire is shown in Fig. 10. It has been installed by G.E.C. in the Ambergate Works of Richard Johnson & Nephew, Ltd., and is the second of its kind to be supplied to the company. The installation comprises three vertical cylindrical furnaces, each rated at 90 kW, and eighteen annealing containers 68 in. deep and 33 in. dia. Twelve of these containers are normally housed in simple brick-lined cooling pits and provision is made for storing six in thermally insulated pits which form recuperators. When a continuous cycle of production is in operation, newly charged annealing containers are placed in the recuperators alongside hot containers recently removed from the furnaces. By this means a new charge can be pre-heated to about 200° C. with a resultant saving in power.

The furnace charge is carried on a base casting which is suspended from an insulated pot head by means of

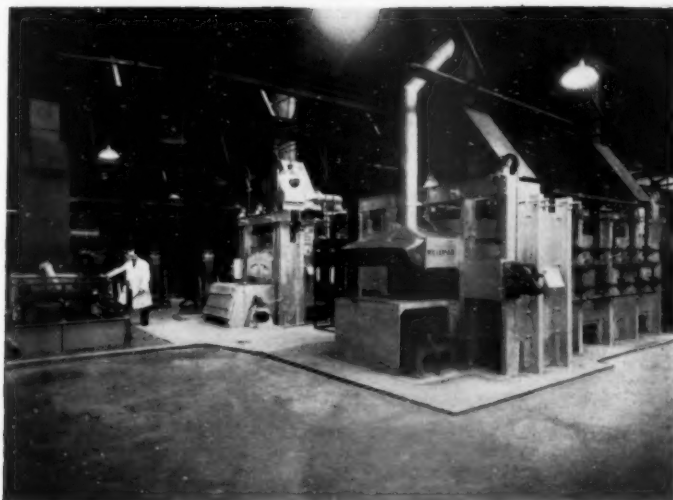


Fig. 13.—A general layout of a hardening, tempering and forming installation, designed and built by The Wellman Smith Owen Engineering Corporation, Ltd., for the heat treatment of steel components.

three heat- and creep-resisting bars. This construction allows the use of a lightweight pot envelope, which allows the rapid transfer of heat from the furnace to the pot and thence to the charge. The pot is closed by clamping the pot head on to a rubber ring fitted into the top of the pot. This assures a gas-tight seal and the rubber ring is cooled by circulating water through a channel round the top of the pot. An average weight of 20/25 cwt. of wire is carried in each pot. An atmosphere of partially-burnt town's gas, supplied by a G.E.C. gas burner, surrounds the charge. The gas is cooled and scrubbed and has its dew point reduced to about -4°C . by means of a separate silica gel drying unit, before it comes into contact with the charges in the pots.

Fig. 11 shows a development which has recently come into operation; it concerns the incorporation of a fan in the charge container in a pit type bright annealing furnace. This improvement has resulted in a significant speeding up of both heating and cooling and has enabled the user to obtain over 50% greater output from his plant; 5 to 10% power economies have also been achieved. The illustration shown with this improvement is a 140 kW pit furnace for bright annealing coil strip at Samuel Fox & Co., Ltd.; it is a Birlee development.

A rectangular bell-type furnace, by G. W. B. Electric Furnaces, Ltd., recently installed for bright annealing cupro-nickel, copper, brass, nickel-silver and other non-ferrous alloys, is shown in Fig. 12. The rating of the furnace bell is 80 kW, arranged in two independent zones, and the average output is 7 to 10 cwt. per hour, the charge of each base, of which there are four, weighing 20 to 30 cwt. As in normal practice, each base is fitted with its gas-tight heat-resisting steel charge retort resting in the sealing trough circumscribing the base. The sealing medium is chrome ore or sand. Protective atmosphere is provided by a regenerative ammonia burner working in conjunction with an ammonia cracker and silica gel driers. The gas storage tanks can be seen in the illustration which shows one base complete with charge and the retort in the raised position. The temperature range of this installation is from 450° C. to



Fig. 14.—An installation of bogie hearth furnaces by Brayshaw Furnaces & Tools, Ltd., for hardening and tempering steel plates.

900° C. and typical power consumptions are as follows :

Nickel silver ..	140/180 kW per ton at 750° C.
Copper and brass ..	115/125 kW per ton at 600° C.
Cupro-nickel ..	160 kW per ton at 700° C.

An average of 0.5 lb. of ammonia per ton of metal treated is consumed. The charge space per base is 4 ft. by 2 ft. by 2 ft. 6 in., and the heating elements are 80/20 nickel-chromium strip.

Hardening and Tempering Furnaces

There are many recent installations of plant for hardening and tempering, and many improvements have been incorporated in them. In low temperature treatment, particularly for tempering, furnaces have been developed in which heating is being applied by the recirculation of burnt gases in large volumes, and at high velocity—the heat being generated in a separately constructed combustion chamber externally located. This system is being applied for a variety of purposes where accurate temperature distribution is of special significance as in the case of alloy steels and aluminium alloys.

Among recent installations is one for hardening, tempering and forming steel components, designed and constructed by The Wellman Smith Owen Engineering

Corporation, Ltd. This installation, a general layout of which is shown in Fig. 13, comprises hardening and tempering furnaces, each of the conveyor hearth type and equipped with automatic temperature control, forming machine and quenching equipment.

The hardening furnace, having a width of 4 ft. 6 in. and length of 13 ft. 6 in., is designed for an output of approximately 8½ cwt. per hour of steel components heated to 950° C. It is fitted with a horizontal plate-type conveyor, constructed of heat-resisting steel, having a speed of 60 ft./hour. Town's gas at 450 B.T.U./cu. ft. is used for firing; a gas consumption of 6,655 cu. ft./hour was allowed for in order to meet peak requirements. The furnace is fitted with eight 5-therm Wellman burners, the combustion air being supplied by an electrically driven fan operating at a pressure of 8 in. W.G. The products of combustion are exhausted from the furnace through equally distributed ports at hearth level (damper controlled) and discharged to atmosphere through up-takes built into the furnace side walls. The tempering furnace, with conveyor, deals with the same material, heating up to 500° C., for which 1,800 cu. ft./hour of gas are allowed. This furnace is fitted with eleven 1-therm Universal burners. The control equipment in each furnace consists of an Elliott automatic indicating temperature regulator and an Elliott continuous-chart indicating recorder.

Brayshaw Furnaces & Tools, Ltd., have installed several furnaces which differ fundamentally from ordinary direct-fired furnaces, heating being carried out by the principle of recirculation of burnt gases in large volumes and at high velocity—the heat being generated in a separately constructed combustion chamber externally located and connected to the furnace proper by insulated ducts. The hot products of combustion are constantly recirculated through the work chamber by means of a special powerful fan; the temperature of the chamber being adjusted by burning fresh gases in the external combustion chamber and adding the heat developed to the main body of recirculating gases. By this means it is claimed that even distribution of temperature is rapid and accurate and easily controlled.

Examples of these furnaces are shown in Figs. 14, 15, and 16. The first shows an installation of bogie hearth furnaces for hardening and tempering steel plates. The tempering furnace in the centre having a bogie hearth

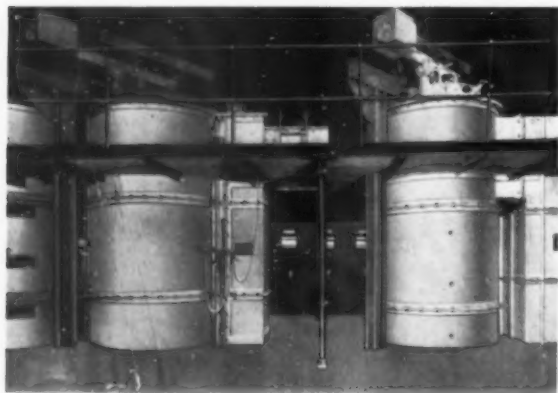
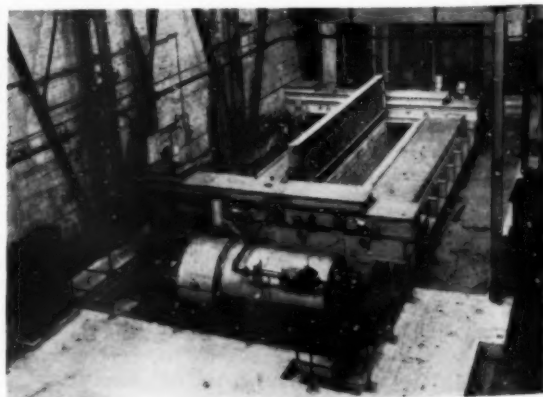


Fig. 15.—Vertical pit-type hardening and tempering furnaces, with chambers 4 ft. dia. and 22 ft. deep, by Brayshaw Furnaces & Tools, Ltd.



Courtesy of Messrs. Thos. Firth & John Brown Ltd.
Fig. 16.—Triple-chambered pit-type hardened steel roll tempering furnace. (Brayshaw Furnaces.)

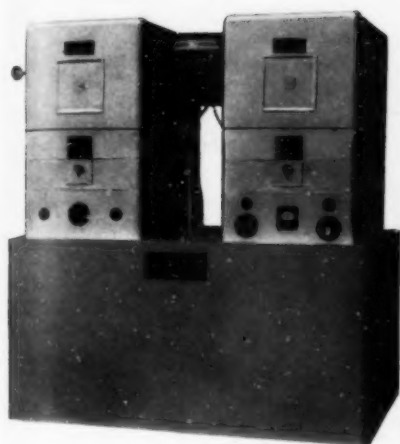


Fig. 17.—High speed steel hardening furnace, with two self-contained chamber units, designed and constructed by Messrs. Wild-Barfield Electric Furnaces, Ltd.

8 ft. wide and 20 ft. long, is heated by recirculated products. Fig. 15 shows an installation of vertical pit-type hardening and tempering furnaces with chambers each 4 ft. dia. and 22 ft. deep, the tempering unit on the right being heated entirely by recirculated products. Fig. 16 shows a triple-chambered pit-type hardened steel roll tempering furnace, heated by recirculated products, arranged with three working chambers, each 4 ft. deep and 22 ft. long, two of the chambers being 3 ft. wide and the other 3 ft. 6 in. wide. This particular furnace is designed as a twin unit the two smaller chambers being heated independently of the larger chamber, separate combustion chambers being arranged at each end of the furnace for this purpose. This unit has been designed to allow for two separate temperatures to be worked simultaneously if necessary, or, alternatively, when production does not warrant the full plant in operation, either the small chambers or the large chamber can be shut down. Insulated box type covers, of hinged type and counterbalanced, are fitted to each work chamber, and are electrically operated and controlled by push button mechanism.

Fig. 17 shows the clean lines and neat appearance of a high speed steel hardening furnace by Wild Barfield Electric Furnaces, Ltd., which embodies a number of interesting features. The furnace comprises two self-contained chamber units, each having its own separate control unit contained within its base. The preheating chamber, lined with high grade insulating bricks, has elements of nickel-chromium in coil form and carried in grooved refractories forming the roof, hearth and side walls. A heat resisting hearth tray is fitted. The maximum operating temperature of this chamber is 940°C . and the furnace is rated at 4 kW. The hardening chamber, also lined with insulating brick, has silicon carbide heating elements in the side walls, with external connections in adequately protected ventilated compart-

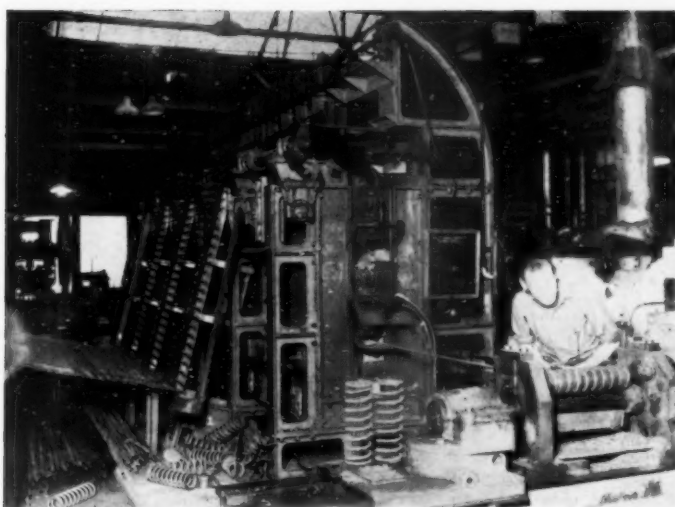


Fig. 18.—Vertical slot furnace specially designed by The Incandescent Heat Co. Ltd., for the heat treatment of bars, tubes, sections and narrow strip.

ments. A renewable refractory hearth tray is fitted. The maximum operating temperature of this chamber, which is rated at 5 kW, is $1,350^{\circ}\text{C}$. Both chambers have insulated, spring-operated, vertical-lifting doors, incorporating a door switch that isolates the heating elements from the main electrical supply when the doors are opened. Each chamber is provided with a Paragen burner equipment for atmosphere control. Both chambers have wide range energy regulators for temperature control, pilot lamps and main relays. The hardening chamber is also provided with an element connection rotary switch, ammeter and magnetically operated circuit breaker, the combination of which extends the useful life of the elements.

High thermal efficiency, great economy of floor space, simplicity in operation, which may be completely automatic if required, are the claims for the vertical slot furnace shown in Fig. 18. It has been specially designed by The Incandescent Heat Co., Ltd., for the heat treatment of bars, tubes, sections or narrow strip, from a few feet up to 50 ft. or more in length. This furnace will charge itself automatically, by side charge conveyor, whether the piece is a few feet or 50 ft. long. It will accept into its conveyor mechanism bars, tubes or sections with reasonable variation from the straight. It will heat or reheat bars, tubes, sections or narrow strip at temperatures up to $1,000^{\circ}\text{C}$., and discharge piece by piece at high speed at any frequency required. It will operate on conditioned furnace atmospheres for critical surface finish. This furnace is claimed to give doubled output for the same shop floor area as compared with horizontal end or side charge furnaces, to effect a saving in fuel consumption of 25 to 50% depending upon throughput and class of work, and to operate as a completely automatic thermal machine requiring minimum supervision and operating skill.

Nearing completion at the Dagenham Works of The Ford Motor Company are two double-deck hardening and tempering furnaces for axle shafts (Fig. 19); the rating is 300 kW distributed in eight independently controlled zones. The axles, supported on shoes, are loaded on the

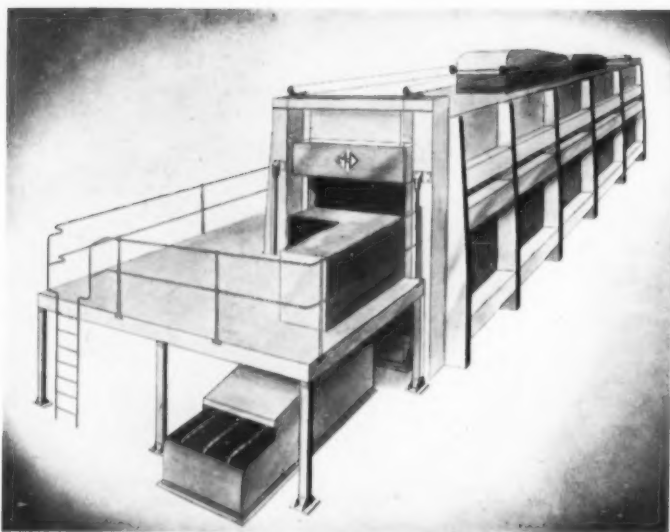


Fig. 19.—Sketch of double-deck hardening and tempering furnace by McDonald Furnaces, Ltd.

top deck and automatically pushed through the hardening chamber. Each axle is selected and automatically discharged into a receiving trough for the operator to spin quench. The shoes, when empty, are discharged on to a hoist, which is interrupted during its descent to allow for loading of axles already hardened. The loaded shoes are then pushed through the tempering chamber. On emerging at the discharge end, the loaded shoes pass on to a second hoist, and tipping levers which operate as the hoist commences to lift cause the axles to be discharged on to a water spray quench conveyor. Pushers, hoists and the discharge door of the hardening furnace are synchronised with the tipping mechanism and are automatically controlled by the master switch gear motor panel which has an infinitely variable time setting between limits. Many features of the design, including the construction of the furnace casing, form the subject matter of patents pending.

The semi-continuous furnace, shown in Fig. 20, is designed for the precipitation hardening of light alloy pistons by G. W. B. Electric Furnaces, Ltd.; it is rated at 70 kW. The heater unit is mounted in the roof and supplies heat to the chamber by means of ducts. The recirculation fans fitted in the roof, and the adjustable dampers, ensure a high degree of thermal uniformity. The furnace is provided with two vertical sliding doors, one at each end, to allow for semi-continuous operation by means of the charge trucks. Four of these trucks, each carrying a charge basket 40 in. high and 33 in. dia., and accommodating 0.5 ton of light alloy pistons, can be used in the chamber at one time. In this instance, the operating temperature is 180° C.

The demand for high temperature furnaces capable of operating at temperatures up to 1,400° C. continues. A furnace which has been successfully used for this purpose is an electric-resistance furnace, incorporating Silit heating

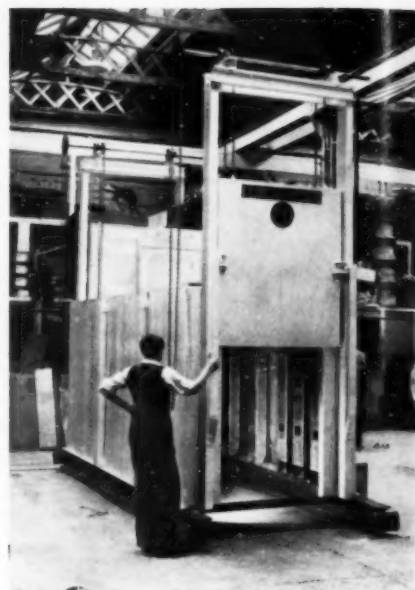


Fig. 20.—A semi-continuous furnace, designed by G. W. B. Electric Furnaces, Ltd., for the precipitation hardening of light alloy pistons.

rods, made by Siemens-Schuckert (Great Britain), Ltd. Silit consists of silicon carbide, a material which is capable of operating at higher temperatures than the metals used for the heating elements of the majority of electric furnaces. As with all carbide compounds, the electrical resistance of Silit increases somewhat in the course of its life, a phenomenon known as ageing. The increase is much less than with other silicon carbide materials; most of it occurs in the first 60-80 hours and a voltage reserve at the transformer of only 40% is ample to cover the ageing. A salient feature of Silit heating rods is that the glowing portion is in one

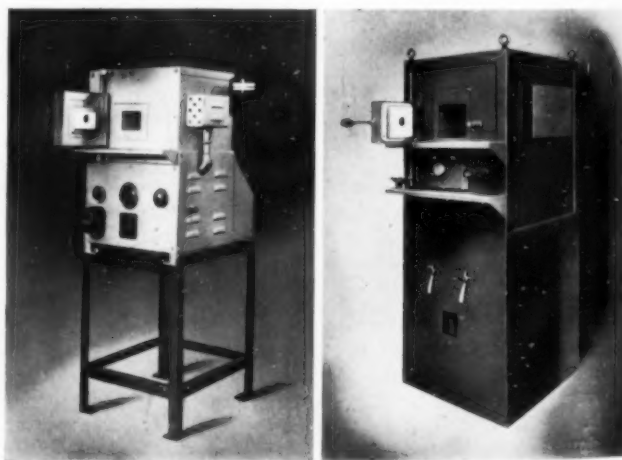


Fig. 21.—Siemens-Schuckert furnaces utilising Silit heating rods. Left, high-temperature laboratory furnace and, right, a double muffle furnace for hardening high-speed steel tools.



Fig. 22.—The Birlec gas fired radiant tube pit furnace installed at the works of British Timken, Ltd.

piece with the ends which pass through the furnace walls, thus avoiding butt joints. A high-temperature laboratory furnace and a double-muffle furnace are illustrated in Fig. 21. The former is designed to operate at muffle temperatures up to $1,400^{\circ}\text{C}$. whilst the double-muffle furnace is primarily intended for hardening high speed steel tools. The lower muffle is used for preheating and has, in consequence, a maximum temperature of 900°C ., with nickel-chromium wire elements. The temperature of each muffle is individually controlled, either by hand or automatically, as required.

Gas Carburising Equipment

The carburisation of steel may be carried out using solid, liquid, or gaseous media, and although probably the means most widely used is that of solid carburisers, the advantages that accrue from gas carburising have resulted in that method making rapid progress, particularly where large components requiring relatively deep cases have to be treated, and precise control of the case is essential. An interesting installation of this kind is a gas-fired, pit-type carburising furnace mounted in a pit 13 ft. deep, so that the top plate is at floor level, the charge, supported on a suitable carrier, being handled by means of an overhead crane, which traverses the

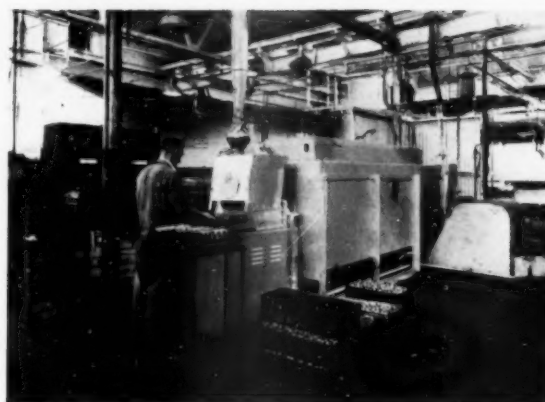


Fig. 23.—A Birlec 35 kW continuous gas carburising furnace.

furnace, quench tank, and loading and unloading stations. Unlike the conventional design, this furnace has a gas-tight external casing and lid, and the carburising atmosphere is allowed to come in contact with the heating elements. The use of the specially chosen refractory materials resistant to attack by carburising gases, in conjunction with the radiant tube heating elements, has made this construction possible. This furnace is installed at the works of British Timken, Ltd., and is shown in Fig. 22. It is a Birlec design and incorporates the Birlec patented recuperative radiant tube, in which gas and primary air are fed to a burner at one end of the tube, while secondary air, preheated by means of a small recuperator, is fed to the other. By adjustment of the secondary air supply, exceptional temperature uniformity along the length of the tube is obtained.

The carburising gas is a mixture of conditioned town's gas and butane. A circulating fan, located at the bottom of the furnace, provides for adequate gas circulation. A cylindrical baffle of heat-resisting material surrounds the charge space, and guides the gas upwards over the heating elements, and downwards through the charge. A small Birlec 35 kW continuous furnace, shown in Fig. 23, has recently been put into operation for gas carburising.

A typical example of gas carburising plants by The Incandescent Heat Co., Ltd., is shown in Fig. 24. In conjunction with The Lithium Corporation of the United States, this firm uses lithium in carburising with great success. The furnace is a typical lift-out type and is applied to carburising heavy gears, etc. It is the Incandescent "Spiro-Ray" type and has three bases. While a load is being carburised on one base, another is being cooled, while the third is being loaded. The installation includes a quench tank provided with rapid oil circulation; the load may thus be hardened directly after the carburising operation, with a consequent saving in time and fuel necessary for reheating. The plant is provided with an endothermic gas generator and each base has its own Lithanol control panel.

Gas carburising equipment is also being given considerable attention by Wild-Barfield Electric Furnaces, Ltd., and a recent installation is shown in Fig. 25. The equipment is fed with raw town's gas direct from the mains, and prepares it for carburising without additions such as

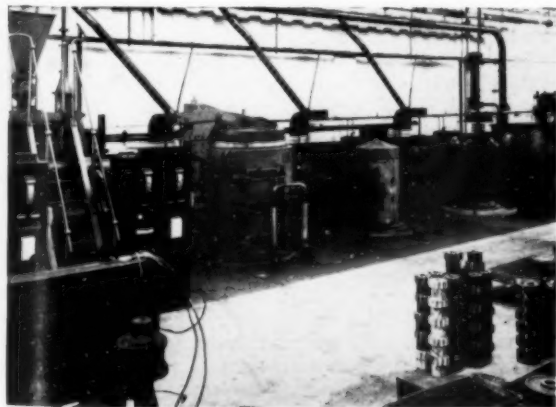


Fig. 24.—A typical lift-off type of plant by The Incandescent Heat Co., Ltd., for gas carburising heavy gears.



Fig. 25.—Gas carburising equipment by Wild-Barfield Electric Furnaces, Ltd.

butane, propane, etc. Deleterious constituents of the town's gas are removed. This prepared gas does not leave a hard carbon deposit on the work; there is no necessity, therefore, to achieve any balance of mixture to minimise sooting, and carburising can proceed at the correct temperature for the steel under treatment. Furthermore, it is claimed that precise control over diffusion enables the "active" carburising to be undertaken at the maximum theoretical rate. The combination of these factors results in faster production with better quality.

The Leeds and Northrup Company has recently introduced Series H Homocarb equipment which provides a practical means of controlling the carbon potential of the furnace atmosphere throughout the entire heating cycle. With Microcarb atmosphere control—an essential feature of this new series—application of the Homocarb method is expanded to include a wide range of heat treatments, from those requiring merely a protective atmosphere to those requiring an actively carburising atmosphere. This new equipment thus becomes a flexible, versatile tool in the hands of the heat treater, enabling him to perform, in one furnace, such diversified operations as hardening, annealing, normalising, carbon restoration, homogeneous carburisation, or carburising to controlled surface carbon concentration, and to perform them more efficiently. Microcarb atmosphere control, through automatic regulation of the flow of Homocarb fluid, enables the heat treater to control the carbon potential of the furnace atmosphere as easily as he now controls temperature. In this country, the Leeds Northrup Company is represented by The Integra Company, Ltd.

Gaseous Annealing of Malleable Castings

Continuous improvement has taken place since Birlec, Ltd., in 1946, installed the first elevator furnace for the gaseous annealing of whiteheart malleable castings. During the past year, the earlier development work has borne fruit in the number of new installations commissioned; the total number now in service is 24, with an approximate total capacity of 16,500 tons per year. Additionally 14 more furnaces are in various stages of production.

One recent feature has been the simplification of the furnace design, which is favourably reflected in the

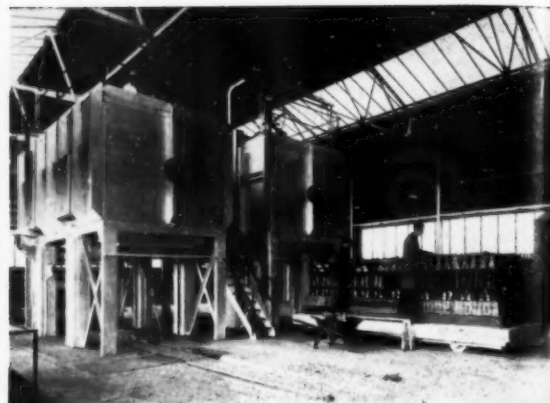


Fig. 26.—Two recently commissioned Birlec furnaces for annealing whiteheart malleable castings at Messrs. Bullers, Ltd.

capital cost, although this advantage is offset by steadily increasing material and labour costs, without affecting the efficiency of the process. Another significant feature has been the successful annealing of heavy section castings. Fig. 26 shows two of these furnaces recently put into commission at Messrs. Bullers, Ltd. By means of an automatic control, a decarburising atmosphere is maintained consistently in the furnace chamber throughout the treatment, thus bringing the material to a suitable malleable form while preserving a scale-free finish. The total cycle time is between 24 and 40 hours, according to the thickness of the castings. The operating temperature is about 1,050° C.

Gas Cyaniding

Gas cyaniding, sometimes referred to as dry cyaniding or carbo-nitriding, may be defined as a process of gaseous case hardening of iron-base alloys by heating in an atmosphere of a composition that allows both carbon and nitrogen to be absorbed into the case in a controlled ratio. The parts are then quenched or air cooled as desired. It can be considered as a modified gas carburising process rather than modified nitriding in as much as the treatment is conducted at a temperature above the upper critical, while the hardening of the case is brought about by the usual austenite-martensite transformation, as in carburising. The difference between the two processes is that the presence of nitrogen lowers the upper critical temperature of the steel and reduces the critical cooling velocity, with the result that the case hardening can be conducted at a temperature lower than is usual in straight carburising and slower quenching speeds can be used.

Unlike nitriding, therefore, the process is applicable to plain carbon steels of carburising quality in addition to the low alloy carburising steels and—depending upon the carbon/nitrogen ratio which, in turn, is controlled by the operating temperature and the atmospheric composition used—surface hardness in excess of that possible in carburising is obtained. Because of the increased hardenability, plain carbon steels may often be substituted for low alloy steels, but in this respect it should be noted that the increased hardenability is restricted to the case.

The plant required consists of an atmosphere generator, similar to that used in gas carburising, but including

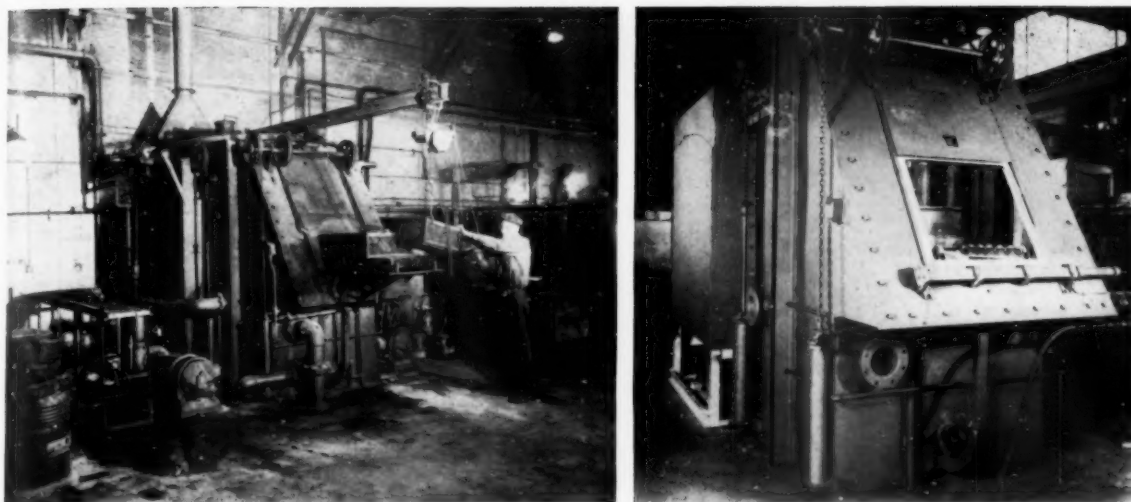


Fig. 27.—Gas cyaniding furnace by Electric Resistance Furnace Co. Ltd. (Left) showing the charging boggles positioned ready for insertion into the vestibule. (Right) shows the vestibule door open with boggles positioned in the heating chamber.

provision for the introduction of ammonia into the atmosphere line, together with a furnace, which may be either a conventional gas carburising furnace or, preferably, a specially designed gas cyaniding furnace (as shown in Fig. 27) which provides for oil quenching of the parts out of contact with the atmosphere. It should be noted that water quenching, even on the very low carbon steels, is not required. The general construction of a gas cyaniding furnace by the Electric Resistance Furnace Co. Ltd., is shown in Fig. 28.

Furnaces for gas cyaniding may be either of the batch or continuous type. Usually, where a quench or isothermal treatment is given to the material after gas cyaniding, the bath is made an integral part of the furnace so that the work is maintained in the atmosphere right up to the time of immersion. An outline drawing of a continuous furnace by General Electric Co., suitable for gas cyaniding followed by isothermal treatment is shown in Fig. 29. Recirculation of the gases within a continuous furnace is essential and suitable gas locks must be provided to protect the furnace atmosphere during charging and discharging.

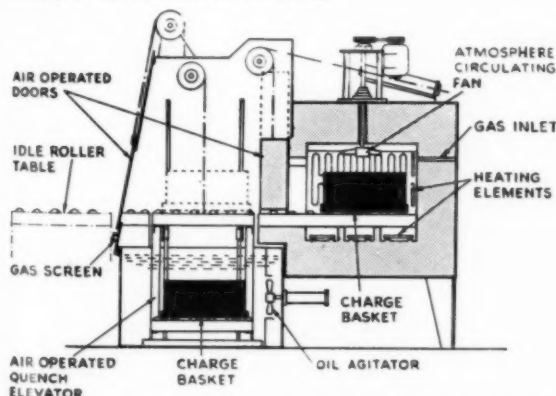


Fig. 28.—A diagram showing the general construction of the gas cyaniding furnace by Electric Resistance Furnace Co., Ltd.

Although resistance to wear is a difficult property to measure, it appears justifiable to say that the wear resistance of gas cyanided parts is greater than that of box or straight carburised parts, even where the surface hardness, as measured, appears to be no greater. The cause of this increased wear resistance may be due to the presence of nitrogen in the martensite case and/or the presence of a small amount of retained austenite.

Salt Baths

In the development of salt baths for surface hardening or casehardening to greater depths, the emphasis has recently been on improved economics of working and better working conditions. Low strength cyanide baths containing 15–20% sodium cyanide are finding increased use in surface hardening mild steel or medium carbon alloy steels. An improved graphitic cover has been developed for use on "Rapideep" baths or higher strength cyanide baths (containing 40–50% sodium cyanide) employed for carburising up to depths of 0.06 in. or more. This graphitic cover reduces loss of bath strength and thus reduces the amount of fresh salt required to regenerate the bath, resulting in greater economy in working. Improved ventilation and protection from salt splashes are obtained by total or partial enclosure of furnaces and quenching tanks, with suitable fume extractors direct to atmosphere, or to a washer which removes fume.

Fig. 30 shows a new design "Cassel" plant in which furnace and quenching tanks are totally enclosed. This design must follow the lines of the automatically-operated "T" type "Cassel" furnace but, for the sake of reduced capital cost, transfer mechanisms are operated manually by handwheels. Work to be treated is charged through a chute into a ladle immersed in the cyanide bath; discharge from furnace to quench is done by operating a counterbalanced handwheel which swings the ladle over the quench tank and empties the parts into the quench. By turning a second handwheel, work is transferred from the quench, through a swinging door in the side of the canopy, into a waiting container.

Fig. 31 shows an I.C.I. (Cassel) automatically-operated

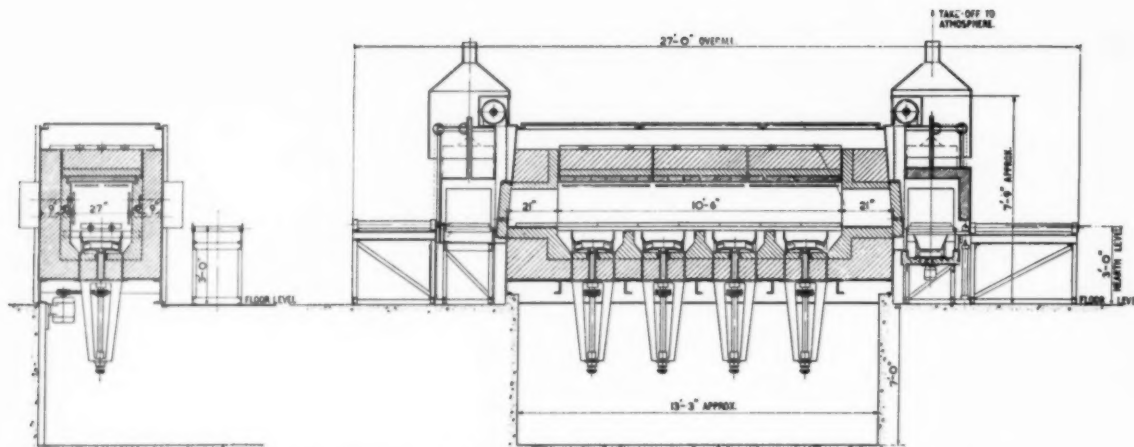


Fig. 29.—An outline drawing of a G.E.C. carbo-nitriding furnace for continuous operation.

C.A. Type plant which is totally enclosed. This is used for austempering large numbers of small, 0.70% carbon steel parts. The parts are loaded in jigs on a conveyor and are transferred by automatically-operated swinging arms through a pre-heat, salt bath at 800° C. for austenitising, and an agitated salt bath at 280/300° C. for quenching and transformation, followed by water quench, hot water wash and air dry. The quenching/transformation bath is fitted with a pump, and a salt filter to remove salt carried in from the austenitising bath, so keeping the quenching bath in a fluid condition.

Nitriding

A battery of nitriding furnaces by G. W. B. Electric Furnaces, Ltd., is shown in Fig. 32. In this installation the charges consist of aeroplane engine crankshafts which are placed in nitriding boxes, sealed and inserted into the furnace. Some applications need up to a 100-hour heating cycle, and during the whole period there must be complete atmosphere control within the nitriding box. In these furnaces, the G.W.B. atmosphere circulating system operates within the box itself and, apart from ensuring temperature uniformity, intimate contact

between the atmosphere and all faces of the charge is attained. Each furnace is divided into two heating zones with a total rating of 80 kW. Automatic control of both furnace temperature and of the atmosphere within the nitriding boxes is supplied, the electrical control gear being shown on the right of the illustration.

Steam Treatment of Tools

Equipment has been developed which is applied for the steam treatment of twist drills. It is claimed that such tools, after having been subjected to this treatment, have an enhanced life of some 500–600%. These results have been achieved in a number of tests carried out. Steam treatment has also been successfully applied to the improvement of the wear resistance of cast iron piston rings, and of chilled cast iron valve tappets; to the increase in hardness and compressive strength of powdered iron compacts; and to the clean tempering of hardened bolts, studs, etc. This process is also being applied to the treatment of brass for such purposes as annealing and the stress relief of brass machine fittings.

The furnace modified for this process is the Homo forced-convection heating unit designed by The Leeds



Fig. 30.—A new design "Cassel" plant in which furnace and quenching tanks are totally enclosed.

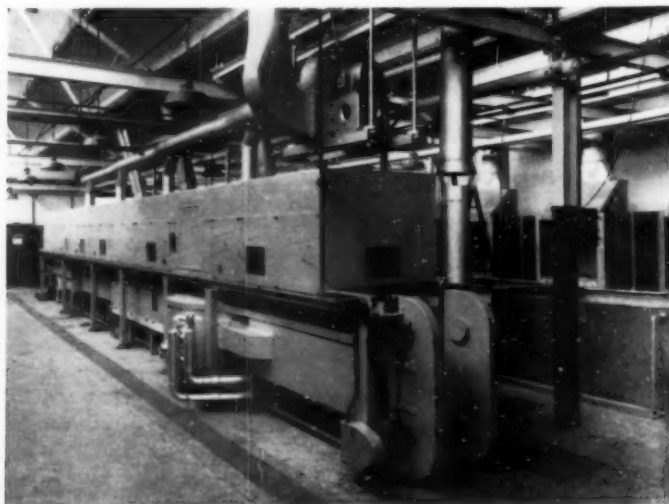


Fig. 31.—An I.C.I. (Cassel) automatically operated C.A. type plant which is totally enclosed.



Fig. 32.—A battery of nitriding furnaces by G. W. B. Electric Furnaces, Ltd.

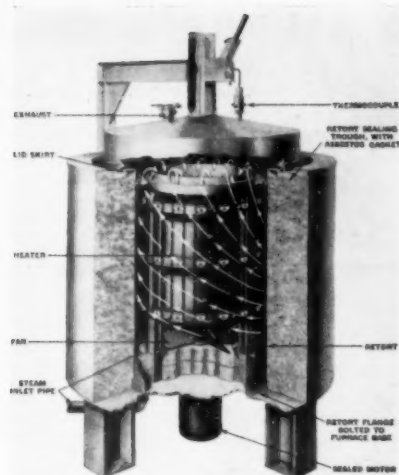


Fig. 33.—A new design Homo furnace primarily developed for the steam treatment of twist drills by The Integra Co. Ltd.

Northrup Company and marketed in this country by The Integra Co. Ltd. A sectional illustration of the steam Homo furnace is shown in Fig. 33; it provides scale-free tempering and stress relief up to 620°C ., and when applied as a final operation to steel and iron components, it imparts a blue oxide finish which has many desirable qualities. When tempering steel or iron parts, the furnace is first brought up to 370°C . with air atmosphere, then held at this temperature for half an hour while steam is fed into the work chamber—purging out all air and removing any danger of rusting. The load is then heated to the soaking temperature and held for the specified time, with steam flowing through the furnace. When handling non-ferrous work requiring lower soaking temperatures, the furnace is purged at 200 to 260°C ., and parts are often quenched in water.

Furnaces for Instructional Work

The importance of heat treatment operations has been recognised for many years in universities and technical colleges and many types of equipment, specially designed for carrying out various treatments, are installed in these establishments. The range of furnaces shown in Fig. 34 shows an installation of gas-fired furnaces which Kasenit Ltd., has supplied to various technical colleges during the past year. The installation covers the heat treatment of both ferrous and non-ferrous metals, including case-hardening and hardening and tempering treatments for high speed steel; also a salt bath for cyaniding. Each furnace can be put into operation at any time to suit students, so as to reach its working temperature within an hour.

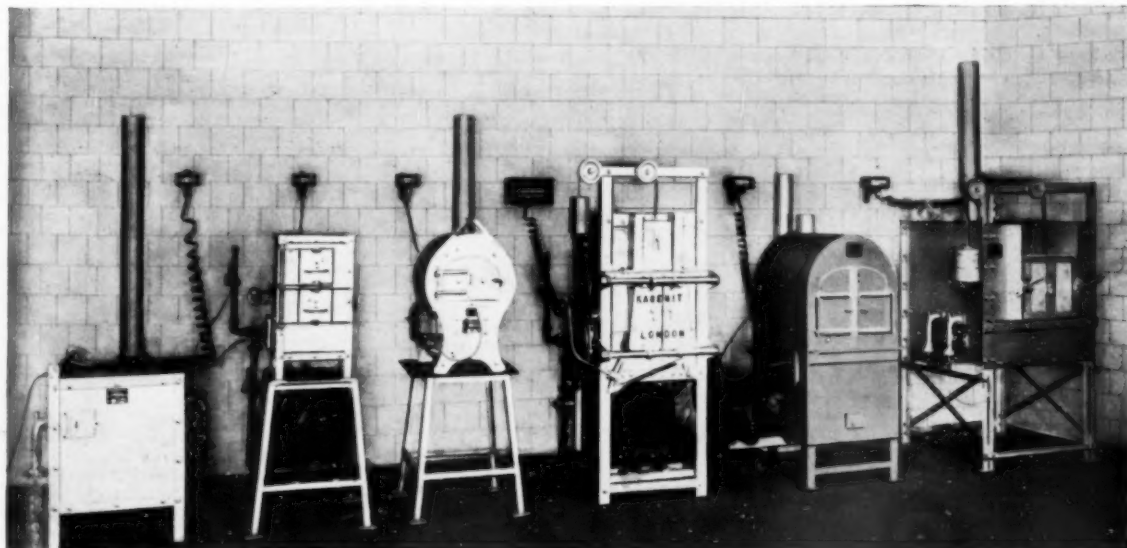


Fig. 34.—An installation of gas fired furnaces by Kasenit, Ltd., supplied to various technical colleges during the year.

Isothermal Transformation Diagrams for Nickel Steels

I.—General Discussion of Diagrams

An extensive study of the isothermal transformation of nickel steels has been made by the Development and Research Department of The Mond Nickel Company, to whom we are indebted for permission to publish this article. The first part deals with general aspects of isothermal transformation diagrams, including methods of determination, factors influencing the shape of the curves, and limitations to be borne in mind in their use. In the second part, to be published next month, reference will be made to the practical application of the information to be obtained from the diagrams, of which those for the more important nickel alloy steels will be presented.

AN isothermal transformation diagram shows the time taken by a steel to transform isothermally, at sub-critical temperatures, from austenite to mixtures of ferrite and carbide. Subject to certain limitations which are discussed later, these diagrams can be of great assistance in increasing the understanding and control of the heat-treatment of alloy steels, for they provide in a unique manner a graphic forecast of the behaviour of steel during heat-treatment. This article provides isothermal transformation diagrams for a selection of the more important nickel alloy steels and the following comments will serve to indicate their significance and method of application.

Determination and Presentation of Isothermal Transformation Diagrams

The most direct of the commonly used methods of obtaining the data for these diagrams is the microscopic method originally used by Davenport and Bain¹. This involves austenitising small samples of the steel at an appropriate temperature, quenching to a sub-critical temperature, holding at that lower temperature for progressively increasing times and then quenching to room temperature. From a microscopical examination of the quenched samples it is then possible to determine the time taken for the reaction to start, the rate at which

it proceeds, and the time taken to complete the reaction. This method is still the most reliable of those available for studying steels which isothermally transform rapidly. It is however, time-consuming and considerable skill is required to interpret the large number of microstructures which it is necessary to examine in the preparation of a diagram. It is, consequently, often more convenient to follow the course of transformation by measuring the changes in some physical property accompanying transformation and, since the breakdown of austenite is accompanied by an expansion, and changes of length are readily measured, the dilatation method is by far the most widely adopted. The isothermal diagrams presented in the recent Iron and Steel Institute Atlas² were determined by the combined application of the dilatation and microscopic methods. Techniques involving the measurement of changes in magnetic permeability³, electrical resistance⁴, and hardness^{3,5}, have been used by other investigators, but these and the dilatation method, when used alone, do not provide the detailed information obtainable from the microscopic method. For example, they do not usually

2 "Atlas of Isothermal Transformation Diagrams of B.S. En Steels." *Iron and Steel, Inst. Special Report No. 40*, 1949.

3 Smith, H. A. "Reactions in the Solid State. I.—Initial Course of Sub-critical Isothermal Diffusion Reactions in Austenite in an Alloy Steel." *Trans. Amer. Inst. Min. Met. Eng.*, 1935, vol. 116, pp. 342-62.

4 Rote, F. B., Truckenmiller, W. C., and Wood, W. P. "Electrical Resistance Method for the Determination of Isothermal Austenite Transformations." *Trans. Amer. Soc. Metals*, 1942, vol. 30, pp. 1,359-73.

5 Rickett, B. L., and Kristufek, F. C. "The Microstructure of Low Carbon Steel." *Trans. Amer. Soc. Metals*, 1949, vol. 41, pp. 1,113-41.

1 Davenport, E. S., and Bain, E. C. "Transformation of Austenite at Constant Subcritical Temperatures." *Trans. Amer. Inst. Min. Met. Eng.*, 1930, vol. 90, pp. 117-54.

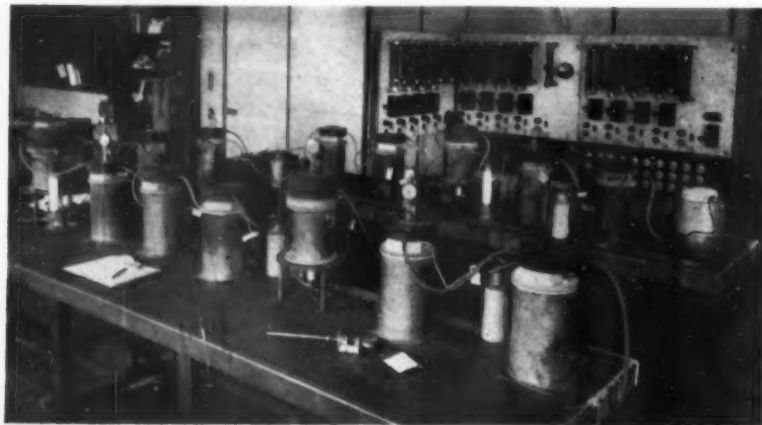


Fig. 1.—General view of equipment used for the determination of isothermal transformation diagrams at the Birmingham Laboratory of The Mond Nickel Company Limited. One of the dilatometers employed will be seen on the bench, centre. In the upper left-hand corner will be seen a cine camera and a battery of lights which were used for automatically recording the progress of transformation. The panel (top right) was specially constructed in the Laboratory to control automatically the temperature of each of the transformation baths over long periods to an accuracy of $\pm 2^\circ \text{C}$.

differentiate reliably between the separation of pro-eutectoid constituent and of pearlite and there is often some uncertainty as to whether a transformation has proceeded to completion or has stopped at some stage of partial transformation. Consequently, it is customary to conduct a few supplementary tests using the microscopic method.

Heal and Mykura⁶ have recently demonstrated the possibility of following transformations by measuring, as transformation proceeds, the changes in the intensity of a line in the X-ray diffraction pattern of either the γ or α phase. This method, although somewhat cumbersome experimentally, has the attractive feature of being even more direct than the microscopic method, and offers the possibility of providing information not otherwise obtainable.

The results of the experimental observations at a series of sub-critical temperatures are usually presented on a single diagram, the ordinates and abscissae of which represent respectively the temperature of transformation and the time. The latter is almost invariably plotted on a logarithmic scale in view of the wide range of transformation times involved. Smooth curves are drawn through points indicating the time required for transformation to start at different temperatures and through those indicating the time required for complete transformation. Additional curves may be drawn to indicate the times required for various percentages of transformation. The A_{e3} , A_{e1} and M_s temperatures of the steel are usually indicated by horizontal lines but the lengths of the lines used for this purpose have, of course, no significance.

It is possible to include on the diagram additional curves to outline the range of temperatures and times within which ferrite, as distinct from ferrite-carbide aggregates, is precipitated. For example, the production of pro-eutectoid ferrite is sometimes distinguished from the separation of pearlite.

Procedure Adopted

The following procedure was adopted by the Research Laboratory of the Mond Nickel Company to determine the diagrams presented in this article.

Specimens.—All samples were taken from batches of commercial steel, the analyses, grain sizes and methods of manufacture of which are quoted beneath the diagrams. Specimens were hot-rolled and cold-drawn to 9 s.w.g. wire or 0.030 in. tape.

Determination of Data.—Each specimen was austenitised for thirty minutes, the temperature adopted being generally at or near the centre of the range quoted in the appropriate B.S. En specification. The diagrams for the more rapidly transforming steels (B.S. En 12, 111 and 160) were determined wholly by the microscopic method. Those for the more slowly transforming steels were derived from a consideration of dilatation curves and the micro-structures of samples quenched after being allowed to transform to various extents. No test extended beyond twenty-four hours. A detailed description of the type of dilatometer used has been published elsewhere⁷, and a general view of the dilatometers and other accessory equipment at present in use is provided by Fig. 1.

Presentation of Isothermal Transformation Data.—The method adopted in this article for the presentation of the diagrams is substantially conventional. The time-scale is logarithmic and is based on seconds, but for convenience, is marked in minutes and hours.

Other Data.—In addition to the details mentioned above, the hardness values developed by the steel when isothermally transformed at each of a series of temperatures are presented. In those cases where transformation had not been started or was incomplete after twenty-four hours, the hardness values are those of the structure developed by holding at the selected temperature for twenty-four hours and then quenching to room temperature. For example, after twenty-four hours at 650° C., the B.S. En 23 steel had transformed only 15% and on quenching to room temperature, the remaining 85% of the structure transformed to martensite. Thus, although the product of transformation at 650° C. was of low hardness, the final structure had a relatively high hardness of 630 D.P.N. On the other hand, this steel transformed completely at 600° C. The room temperature structure contained no martensite and the hardness value of 270 D.P.N. quoted in this instance represents the room temperature hardness of the structure developed at the transformation temperature.

General Features of Isothermal Transformation Diagrams

Isothermal transformations proceed by processes involving nucleation and growth of nuclei. If a sample steel is austenitised and quenched to a sub-critical temperature, then for a definite period of time after the sample reaches temperature there will be no microscopically detectable sign of transformation. This initial period is usually referred to as the "incubation period," or "period of induction." At the end of the incubation period, nuclei are visible in the structure and transformation proceeds by the growth of these nuclei, and of course, by the appearance and growth of additional nuclei.

The type of structure formed depends primarily on the temperature at which the transformation occurs, but is also influenced, to some extent, by the composition of the steel. It will be convenient to discuss the general features of an isothermal transformation diagram by referring to the diagram for the medium carbon 2½% nickel-chromium-molybdenum steel (B.S. En 25) which has been reproduced as Fig. 2.

Between the upper and lower equilibrium transformation temperatures, ferrite alone is formed by isothermal transformation. The separation is preceded by an incubation period and proceeds by nucleation and growth, but all of the austenite does not transform. The reaction ceases when the austenite and ferrite are present in the proportion required by the equilibrium diagram at the temperature involved.

In the temperature range between the A_{e1} temperature and 570° C. transformation occurs in two stages—precipitation of ferrite, followed by the formation of pearlite. The amount of ferrite formed decreases as the temperature of transformation is lowered and the amount of pearlite formed increases proportionally. It would thus appear that the carbon content of the pearlite decreases as the temperature of formation is lowered.

The formation of pearlite in the B.S. En 25 steel is

⁶ Heal, H. T., and Mykura, H. Paper to be published in *Jnl. Iron and Steel Inst.*

⁷ Allen, N. P., Pfeil, L. B., and Griffiths, W. T. "Determination of Transformation Characteristics of Alloy Steels." *Iron and Steel Inst.* Second Report of the Alloy Steels Research Committee, Special Report No. 24, section XIII, pp. 369-90 (1939).

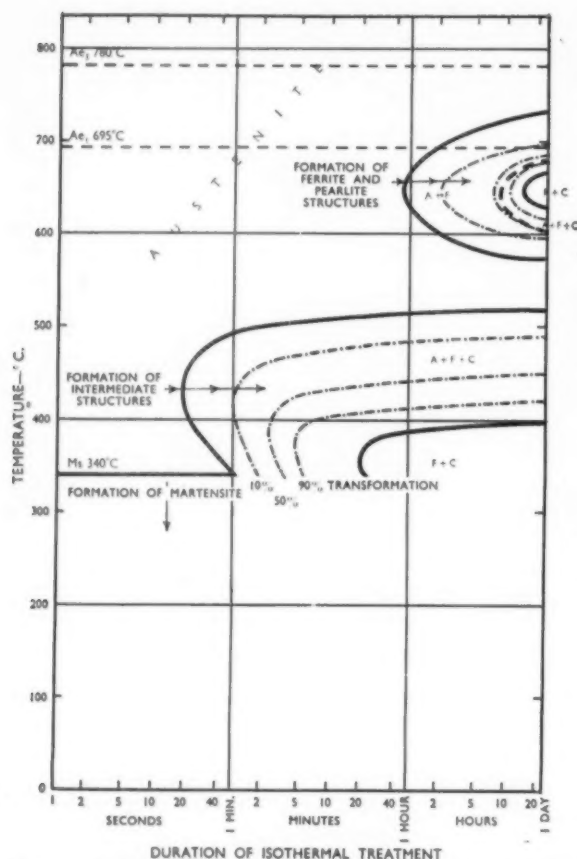


Fig. 2.—Isothermal transformation diagram for a B.S. En 25 steel, austenitised for 30 mins. at 835° C.

always preceded by the separation of ferrite (Fig. 2) but other steels (e.g., En 110, Fig. 8) have a temperature range within which the formation of pearlite is not preceded by ferrite separation. The two-stage nature of the formation of ferrite-pearlite structures is indicated in Fig. 2, and in other isothermal diagrams in this article, by a heavy broken line. This line shows the time at which carbide first appears in the structure. It must be emphasised that this does not necessarily indicate the end of the separation of pro-eutectoid ferrite, for it is very likely that the two stages of the reaction overlap to an appreciable extent. In certain diagrams, where the pearlite and the intermediate reactions overlap, the full extent of this line has not been shown owing to the difficulty of defining its position with adequate accuracy.

The above remarks apply to a hypo-eutectoid steel. The pro-eutectoid constituent in the case of a hyper-eutectoid steel would of course be cementite.

The detailed structure of pearlite varies depending on the temperature at which it is produced. Pearlite formed just below the A_{e1} temperature is readily resolved under the microscope (Fig. 3) and has coarse carbide lamellae which tend to globularise, but pearlites of increasing fineness are formed at lower temperatures and those formed towards the lower end of the pearlite formation range are not readily resolved under a normal metallurgical microscope (Fig. 4). This change in



Fig. 3.—Ferrite and a coarse lamellar pearlite formed by isothermally transforming a sample of B.S. En 111 steel at 700° C. $\times 850$

appearance is accompanied by an increase of hardness.

Fig. 5 shows various stages in the formation of a ferrite-pearlite structure in a high carbon 2½% nickel-chromium-molybdenum steel (B.S. En 26). Figs. 5a and 5b illustrate the early part of the transformation during which ferrite precipitation predominates and Figs. 5c and 5d demonstrate the subsequent separation of pearlite.

Within the range of temperature between the A_{e3} temperature and the lower limit of the pearlite range (570° C. in Fig. 2) the incubation period at first decreases and then increases with decreasing temperature of transformation. Simultaneously the rate of reaction passes through a maximum. That part of the curve at which the incubation period reaches a minimum, is usually referred to as the pearlite "nose" or "knee" and is of considerable importance since its position on the time-scale may determine the hardenability of a steel.

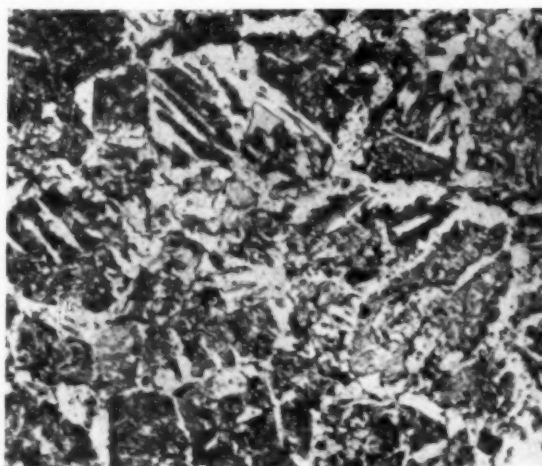


Fig. 4.—Ferrite and fine irresolveable pearlite formed by isothermally transforming a sample of B.S. En 111 steel at 600° C. $\times 850$



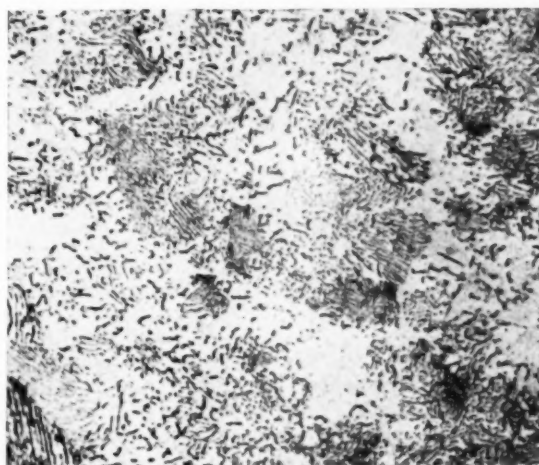
(a) 7 hours



(b) 14 hours



(c) 19 hours



(d) 24 hours

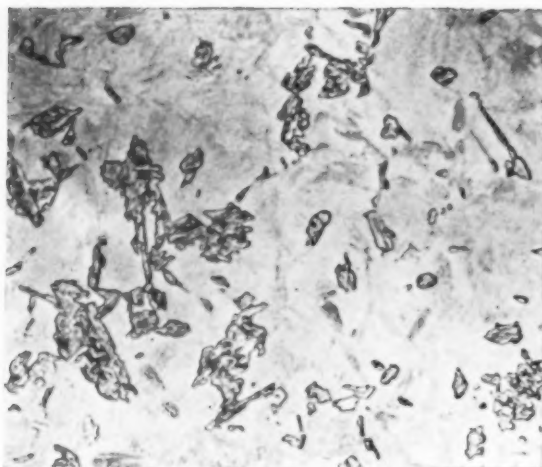
Fig. 5.—Various stages in the formation of a ferrite pearlite structure in a B.S. En 26 steel, austenitised at 835° C. and isothermally transformed for the times indicated at 650° C. × 850

The structures produced in the lower temperature range of transformation (between 520° C. and 340° C., in Fig. 2) are usually referred to as "bainite" or "intermediate" structures. These structures are harder than pearlite and their hardness increases progressively towards that of martensite with decreasing temperature of formation. Intermediate structures vary greatly in appearance, but one characteristic type formed at temperatures towards the upper end of the range (upper intermediate structure) has a feather-like appearance and is developed by the growth of fingers of ferrite followed by the precipitation of carbide. The intermediate structures, formed at lower temperatures, on the other hand, appear to form by the simultaneous separation of ferrite and carbide, and the type most frequently encountered has a dark etching acicular appearance not readily distinguishable from that of tempered martensite. Figs. 6 and 7 show various stages in the development of upper and lower intermediate structures in a B.S. En 26 steel.

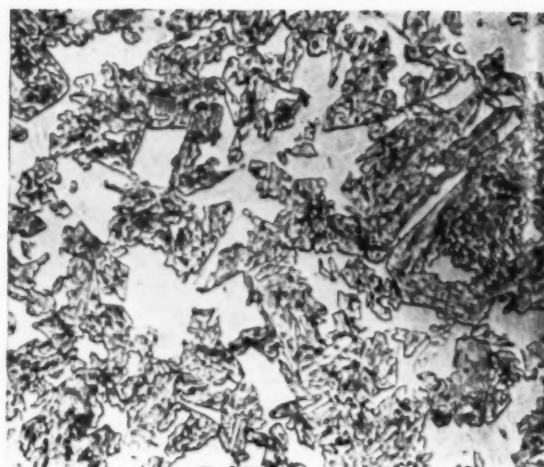
In the diagram (Fig. 2) the pearlite range and the intermediate range are separated by a range of temperature within which austenite is relatively stable. For example, at 540° C. no transformation occurs in 24 hours. This is a normal feature of the diagrams for steels containing appreciable percentages of chromium or molybdenum, but for many steels the two transformation ranges overlap. The diagram for the B.S. En 100 steel (Fig. 9) shows partial coalescence of the two ranges. More complete coalescence is apparent for the B.S. En 22 steel (Fig. 10) and in the diagram for the B.S. En 12 steel (Fig. 11) the two ranges are not readily distinguishable.

Effect of Composition on Isothermal Transformation

The general effect of carbon, and of all the common alloying elements except cobalt, is to move the isothermal transformation curves to the right, that is to delay the initiation and to decrease the rate of transformation.



(a) 1 minute 40 seconds



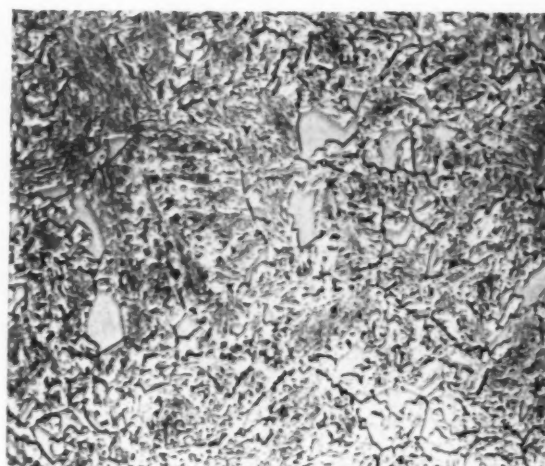
(b) 3 minutes 20 seconds

Fig. 6.—Three stages in the formation of upper intermediate structure in a B.S. En 26 steel, austenitised at 835° C. and isothermally transformed for the times indicated at 450° C. $\times 850$

Increase of carbon content, up to the eutectoid percentage, retards the pearlite reaction but further increase of carbon content decreases the incubation period and increases the rate of reaction. This, it has been suggested, is due to the nucleating action of carbide particles rejected prior to the start of the pearlite reaction⁸. On the other hand, the intermediate reaction is, in general, steadily retarded by progressive increase of carbon content.

Alloying elements differ in the nature and magnitude of their effects on isothermal transformation. Nickel^{8, 9, 10} and manganese^{8, 11} retard the pearlite and the intermediate transformations fairly uniformly at all temperatures. Copper and silicon are similar to nickel in their effects on isothermal transformations, but their retarding effect is much weaker. Cobalt¹² appears to increase the rate of transformations at all temperatures.

Molybdenum^{8, 9, 11, 13, 14} and chromium^{8, 15} strongly retard the pearlite reaction, but affect the intermediate reactions to a much smaller extent. These elements also raise the temperature range within which the pearlite reaction occurs and depress the temperature range for the intermediate reactions. Consequently the isothermal transformation diagrams for steels con-



(c) 1 hour 30 minutes

taining appreciable amounts of either element frequently show a bay of austenite stability between the two reaction zones.

Vanadium usually accelerates transformation at sub-critical temperatures. The carbides of vanadium are relatively insoluble and are not usually taken into solution at normal austenitising temperatures. The carbon content of the austenite of a vanadium-bearing steel is thus reduced below its nominal value, and transformation at sub-critical temperatures is promoted. The undissolved carbide particles may also accelerate transformation by serving as nuclei. Vanadium will retard transformation, however, if taken fully into solution at the austenitising temperature¹⁶.

Boron¹⁷ strongly retards the formation of pro-pearlitic ferrite but has a less marked effect on the rate of formation of pearlite and intermediate structures.

8 Davenport, E. S. "Isothermal Transformation in Steels." *Trans. Amer. Soc. Metals*, 1939, vol. 27, pp. 837-86.

9 Scott, D. A., Armstrong, W. M., and Forward, F. A. "Influence of Nickel and Molybdenum on Isothermal Transformation of Austenite in Pure Iron-Nickel and Iron-Nickel-Molybdenum Alloys containing 0.55% Carbon." *Trans. Amer. Soc. Metals*, 1949, vol. 41, pp. 1,145-64.

10 Sheehan, J. P., Julien, C. A., and Trolano, A. R. "The Transformation Characteristics of Ten Selected Nickel Steels." *Trans. Amer. Soc. Metals*, 1949, vol. 41, pp. 1,165-81.

11 Austin, C. R., and Doig, J. R. "The Suppression of Pearlite in Manganese-Molybdenum Steels." *Trans. Amer. Soc. Metals*, 1946, vol. 38, pp. 336-60.

12 Hawkes, M. F., and Mehl, R. F. "The Effect of Cobalt on the Rate of Nucleation and the Rate of Growth of Pearlite." *Trans. Amer. Inst. Min. Met. Eng.*, 1947, vol. 172, pp. 467-92.

13 Blanchard, J. R., Parke, R. M., and Herzig, A. J. "The Effect of Molybdenum on the Isothermal Subcritical Transformation of Austenite in Low and Medium Carbon Steels." *Trans. Amer. Soc. Metals*, 1941, vol. 29, pp. 317-35.

14 Blanchard, J. R., Parke, R. M., and Herzig, A. J. "The Effect of Molybdenum on the Isothermal Subcritical Transformation of Austenite in Eutectoid and Hyper-eutectoid Steels." *Trans. Amer. Soc. Metals*, 1943, vol. 31, pp. 849-68.

15 Lyman, E., and Trolano, A. R. "Isothermal Transformation of Austenite in 1% Carbon, High-Chromium Steels." *Trans. Amer. Inst. Min. Met. Eng.*, 1945, vol. 162, pp. 196-220.

16 Zimmerman, J. G., Aborn, R. H., and Bain, E. C. "Some Effects of Small Additions of Vanadium to Eutectoid Steel." *Trans. Amer. Soc. Metals*, 1937, vol. 25, pp. 755-80.

17 Dugges, T. G., Irish, C. R., and Carville, N. L. "Effect of Boron on the Hardenability of High-Purity Alloys and Commercial Steels." *J. Nat. Bur. Standards*, 1948, vol. 41, pp. 543-74.



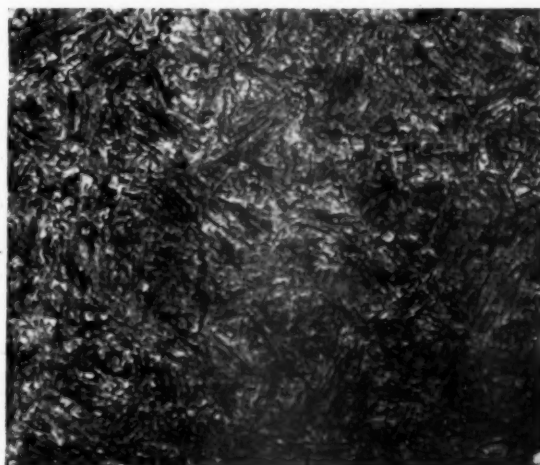
(a) 1 minute 40 seconds



(b) 3 minutes 20 seconds



(c) 5 minutes



(d) 1 hour

Fig. 7.—Four stages in the formation of lower intermediate structure in a B.S. En 26 steel, austenitised at 835° C. and isothermally transformed for the times indicated at 340° C. $\times 850$

Increase of grain size retards the formation of pearlite by reducing the surface area available for nucleation but has little, if any, effect on the rate of formation of intermediate structures¹⁸.

The effects of combinations of two or more alloying elements on isothermal transformations are complex, and a great deal of systematic work is required to determine to what extent the effects of one element are intensified or weakened by the presence of another. There are, however, clear indications that certain combinations are particularly advantageous. For example, Brophy and Miller¹⁹ have shown that nickel retards isothermal transformation to a greater extent in the presence of manganese, chromium or molybdenum than when alone, and that similarly these elements are more effective in the

presence, than in the absence, of nickel. More recently, Hodge, Giove and Storm²⁰ have demonstrated that an addition of 0.3 per cent. molybdenum is about twice as effective in retarding transformation when added to a steel containing 3 per cent. nickel as when added to a steel containing 1 per cent. chromium. A systematic survey of this field should eventually lead to the establishment of the most effective combinations of alloys for different purposes, but so far this aspect of the subject is substantially unexplored.

The Martensite Reaction

The lower end of the intermediate transformation range usually overlaps the temperature range within which austenite transforms to martensite. The upper limit of the martensite range is usually referred to as the M_s temperature and the lower limit as the M_f temperature.

¹⁸ Griffiths, W. T., Pfeil, L. B., and Allen, N. P. "The Intermediate Transformation in Alloy Steels." *Iron and Steel Inst.* Second Report of the Alloy Steels Research Committee, Special Report No. 24, Section XII, pp. 343-67 (1939).

¹⁹ Brophy, G. R., and Miller, A. J. "An Appraisal of the Factor Method for Calculating the Hardenability of Steel from Composition." *Trans. Amer. Inst. Min. Met. Eng.*, 1946, vol. 167, pp. 654-63.

²⁰ Hodge, J. M., Giove, J. L., and Storm, R. G. "The Hardenability Effect of Molybdenum." *Jnl. of Metals (Trans. Section)*, 1949, vol. 1, pp. 218-27.

The martensite reaction is fundamentally different from the pearlite and intermediate reactions. If a sample of steel is austenitised and cooled to a temperature just below its M_s temperature, sufficiently rapidly to avoid transformation in either the pearlite or the intermediate range, then a small fraction of the austenite will transform almost instantaneously to martensite. No further transformation to martensite will occur on holding at this temperature, but if the sample is progressively cooled, additional martensite will form as the temperature falls until transformation is complete. Thus individual needles or plates of martensite are formed from austenite almost instantaneously, but complete transformation can be effected only by cooling through a distinct range of temperature.

As already mentioned the intermediate range usually overlaps the martensite range. Consequently, if an austenitised sample is quenched to a temperature within the martensite range, partial transformation to martensite may be followed by the isothermal transformation of residual austenite to intermediate structure.

Carbon and most of the common alloying elements depress the M_s temperature. The effects of the alloying elements are, however, relatively slight compared with that of carbon. Since low M_s temperatures promote the retention of austenite and the formation of internal stress and quenching cracks, the mild effects in this respect of alloying elements in general, and of nickel and molybdenum in particular, must be regarded as advantageous.

A number of formulae have been proposed for calculating M_s temperatures from chemical composition. One of the more accurate of these is that due to Nehrenberg²², which will serve to illustrate the relative magnitude of the effects of the more common alloying elements.

$$M_s (^{\circ}\text{F.}) = 930 - 540\text{C} - 60\text{Mn} - 40\text{Cr} - 30\text{Ni} - 20\text{Si} - 20\text{Mo}.$$

Thus 1 per cent. carbon depresses the M_s temperature of a steel about nine times as much as 1 per cent. manganese, and manganese in turn has in this respect twice the effect of nickel. Cobalt^{12, 21} has been reported to raise the M_s temperature.

The usefulness of the above formula and other similar formulae for calculating M_s temperatures from chemical composition is limited by the fact that they assume complete and uniform solution in the austenite of all carbon and alloying elements. If a steel contains undissolved carbides at the austenitising temperature, as is frequently the case with steels containing appreciable amounts of strong carbide-forming elements, then the observed M_s temperature will be higher than would be anticipated from the formulae. Micro- and macro-segregation of carbon and alloying elements will lead to similar discrepancies.

The M_f temperature, i.e. the temperature at which the martensite reaction ceases, is more difficult to determine experimentally than the M_s temperature and little is known of the effect on this of different alloying elements. The limited data available suggest that the temperature difference between the M_s and M_f temperatures is

increased markedly by increase of carbon content²³ and slightly by increase of alloy content²⁴. This temperature difference, for steels containing approximately 0.35 per cent. carbon, appears to be of the order of 250° C.

The M_s temperatures indicated on the diagrams of this publication were determined experimentally by the method described by Greninger and Troiano²⁵. Small samples of the steel were quenched from the austenitising temperature to a temperature within the martensite formation range, tempered immediately for a time and at a temperature which would darken the martensite formed (but not cause isothermal transformation), and then quenched to room temperature. The amount of tempered martensite visible in the matrix of "as-quenched" martensite was estimated microscopically and, by a series of similar experiments at progressively higher temperatures, the highest temperature at which martensite formed, i.e. the M_s temperature, was determined.

Retained Austenite

The M_f temperatures of most of the low and medium alloy structural steels, excluding carburised steels, are slightly above room temperature. If, therefore, the martensite reaction proceeds to completion (that is if the M_f temperature corresponds to 100% transformation and not merely to the cessation of the reaction at some stage of incomplete transformation), one would expect no austenite to be retained at room temperature in these steels.

It is, however, an established fact that austenite is frequently retained in such steels at room temperature and it would, therefore, appear that the martensite reaction does not always proceed to completion. This may be a normal characteristic of the martensite reaction, alternatively it may be a secondary effect due to other reactions. For example, the precipitation of ferrite prior to the martensite reaction will increase the carbon content of the parent austenite and thereby depress both the M_s and M_f temperatures. If the M_f temperature is depressed below room temperature, retention of austenite at room temperature might be expected. It is very likely that the precipitation of pro-eutectoid ferrite or the formation of some upper intermediate structure, which would have a closely similar effect, is responsible for at least some of the retained austenite observed in quenched samples.

Inhomogeneity of the steel when in the austenitic condition may also contribute to the retention of austenite. Such inhomogeneity may have persisted from the original as-cast structure or may even be developed by heat-treatment. For example, very short austenitising cycles, such as those associated with welding, may be insufficient to allow complete diffusion of carbon and those zones originally high in carbon content, e.g., pearlite grains, may not be completely dispersed. As a result certain grains in the steel will have lower than average martensite transformation ranges and, if the total magnitude of this and other effects is sufficient, austenite may be retained at room temperature.

The M_s temperatures of many high carbon steels, including certain carburised steels, are below room

21 Chiswick, H. H., and Greninger, A. R. "Influence of Nickel, Molybdenum, Cobalt and Silicon on the Kinetics and Ar³ Temperatures of the Austenite to Martensite Transformation in Steels." *Trans. Amer. Soc. Metals*, 1944, vol. 32, pp. 482-516.

22 Nehrenberg, A. E., in Contribution to Discussion on Grange and Stewart (see below). *Trans. Amer. Inst. Min. Met. Eng.*, 1946, vol. 167, pp. 494-98.

23 Grange, R. A., and Stewart, H. M. "Temperature Range of Martensite Formation." *Trans. Amer. Inst. Min. Met. Eng.*, 1946, vol. 167, pp. 467-93.

24 Payson, P., and Savage, C. H. "Martensite Reactions in Alloy Steels." *Trans. Amer. Soc. Metals*, 1941, vol. 33, pp. 261-75.

25 Greninger, A. R., and Troiano, A. R. "Kinetics of the Austenite to Martensite Transformation in Steel." *Trans. Amer. Soc. Metals*, 1940, vol. 27, pp. 557-62.

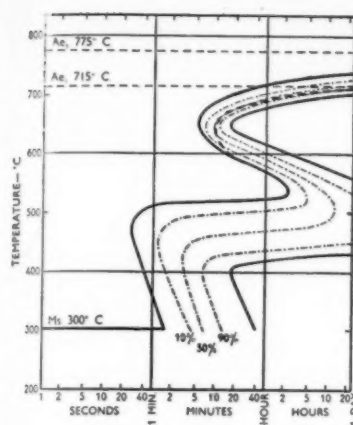


Fig. 8.—B.S. En 110 steel.

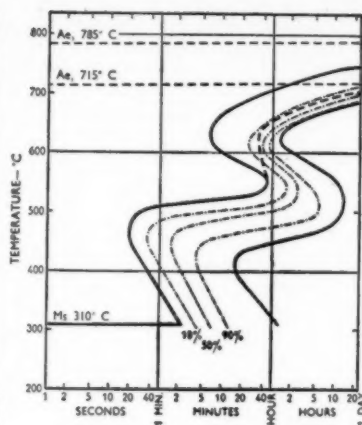


Fig. 9.—B.S. En 100 steel.

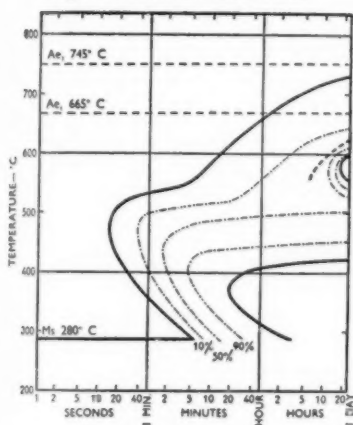


Fig. 10.—B.S. En 22 steel.

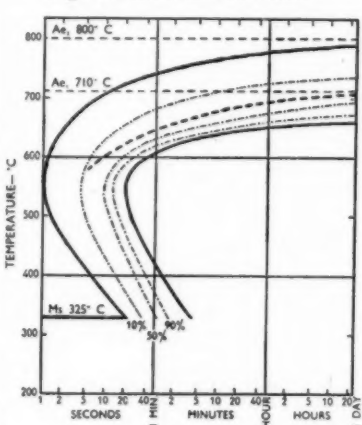


Fig. 11.—B.S. En 12 steel.

temperature. Retention of austenite at room temperature must, therefore, be expected in these steels. If the steel is to be tempered to a relatively low tensile level, the retained austenite will transform during the tempering treatment. If, however, the steel is to be used in a lightly tempered condition, as is, for example, a carburised case, then the tempering temperature will be too low for the effective removal of austenite. In such circumstances sub-zero treatment is the most effective method of removal. During a sub-zero treatment the steel is cooled to below its M_s temperature and the breakdown of austenite to martensite continues with falling temperature in the normal manner.

The retention of austenite and the removal of austenite by sub-zero treatment is complicated to some extent by a phenomenon usually referred to as "stabilisation" of austenite²⁶. If the martensite reaction is interrupted, that is, if cooling from the M_s to the M_f temperature is interrupted for an appreciable time at some intermediate temperature so that the martensite reaction is halted, then the stability of the untransformed austenite increases. When cooling is resumed transformation does not start immediately, as would be expected, but only

after a distinct degree of under-cooling, the extent of which depends on the temperature and the duration of the interruption. Furthermore, in certain circumstances a proportion of the austenite may become wholly resistant to sub-zero treatments.

The phenomenon of austenite stabilisation has been most frequently observed in high-carbon steels but the extent of its occurrence in steels of normal carbon has yet to be adequately assessed.

The Influence of Structure on Mechanical Properties

The best combinations of tensile strength, ductility and impact strength are generally obtained from tempered martensite. The presence in the structure of some ferrite, pearlite or intermediate structure usually reduces the proof stress, the impact strength, the fatigue strength, and in certain instances the elongation and reduction of area values, associated with a given tensile strength. It is, therefore, advisable to avoid transformation to structures other than martensite during the hardening operation. The achievement of this depends on several factors, the more important of which are the transformation characteristics of the steel, the size and the shape of the part to be treated, and the quenching conditions adopted.

The more rapidly the steel transforms, i.e., the shorter the incubation periods indicated by the isothermal transformation diagram, the faster it is necessary to cool the steel to avoid transformation to structures other than martensite. The cooling rates which can be achieved in practice are limited by the size of the component being treated, and thus, although a given quench may be sufficient to harden fully a small bar of steel, it may not be sufficient to harden fully a larger bar of the same steel. The rate at which a steel bar of a given size cools can, however, be increased to some extent, by increasing the severity of the quench, and if no other considerations were involved the most drastic quenching medium would always be used, since this would ensure full hardening to the greatest depth. The steep temperature gradients associated with high rates of cooling, however, increase the dangers of distortion and cracking, and make it advisable to use oil-quenching or air-cooling whenever possible.

Consideration of a selection of isothermal transformation diagrams will show that with some steels the pearlite reaction is more easily avoided than the intermediate reactions, whereas with other steels the reverse is true. By a suitable choice of composition it is usually possible, however, to retard the pearlite transformation sufficiently to avoid the formation of this structure when the steel is hardened even in the largest sizes. Transformation to intermediate structures is, on the other hand, less easily avoided, and unless highly alloyed steels are used

²⁶ Hark, W. J., and Cohen, M. "Stabilisation of the Austenite-Martensite Transformation." *Trans. Amer. Inst. Min. Met. Eng.*, 1949, vol. 180, pp. 47-70.

it is usually necessary to tolerate the development of some intermediate structure towards the centre of medium to large sections. Fortunately the intermediate structures, particularly the lower intermediate structure, affect mechanical properties to a much less marked extent than does pearlite.

Limitations of Isothermal Transformation Diagrams

Certain limitations of isothermal transformation diagrams should be borne constantly in mind.

Each diagram is based on a study of samples taken from a single cast of steel. Other casts of the same type of steel may, because of their different carbon and alloy contents, differ substantially in their transformation characteristics although conforming to the chemical requirements of the specification. Particularly wide variations are to be expected from steels likely to contain variable amounts of residual alloying elements.

It should also be remembered that the small samples used for determining isothermal transformation diagrams may not be representative of the cast as a whole. The transformation characteristics of other parts of the cast may be significantly different. Wide differences have been shown to exist between the transformation characteristics of different points across the section of billets and bars of ordinary commercial steel²⁷. These differences are probably at a maximum in castings and are believed to be progressively reduced by forging and

rolling. At the best, an isothermal transformation diagram shows the average transformation characteristics of the cast and certain zones will usually transform more rapidly and others more slowly than the diagram would suggest.

The isothermal diagrams of many steels are not appreciably affected by quite wide variations of the austenitising temperature, but if the steel contains appreciable percentages of strong carbide-forming elements the effect may be significant. Raising the austenitising temperature of such a steel causes progressive solution of alloy carbide. This alters the composition of the austenite which in turn affects the transformation characteristics of the steel at sub-critical temperatures. Similarly, varying the austenitising time at a given temperature may modify the transformation characteristics, although the magnitude of this effect is appreciably less.

Provided these limitations are appreciated, isothermal transformation diagrams can be of great assistance in increasing the understanding and control of the heat-treatment of alloy steels, for they provide, in a way which no other type of diagram can, a chart which enables one to visualize and anticipate how the steel will behave during heat-treatment.

To be continued

27 Bucknall, E. H. "A Note on the Effect of the Location of the Test-Piece on the Jominy Hardenability of Billets." Symposium on the Hardenability of Steel. *Iron and Steel Inst.* Special Report No. 36, pp. 120-31 (1946).

Magnesium at Ideal Home Exhibition

THE potentialities of magnesium base alloys have long been recognised with respect to their use in structures of a purely mechanical-engineering nature, and in aeronautical construction they have demonstrated their usefulness, resulting in increased stiffness and rigidity, improved safety factor at no increase in weight over aluminium, and simplification of design for production.

An ever increasing tonnage is being used in the aircraft industry but for security reasons the more interesting developments using magnesium in aircraft are not at present available for publication. A new extension in popular use was, however, shown at the Crystal Palace Feature at the "Daily Mail Ideal Home Exhibition." Designed by James Gardner, O.B.E., the feature was built up mainly in magnesium alloy from thin gauge tubes, with cast magnesium alloy intersections and decorative tracery.

The majority of the magnesium castings which formed the intersections and decorative tracery were supplied to Messrs. J. Starkie Gardner, Ltd., the general contractors for the feature, by Messrs. Essex Aero, Ltd., one of the pioneer firms and largest users of magnesium sheet in Great Britain. During and since the war this firm has specialised in the production of magnesium alloy tanks and many other components for the aircraft industry. Essex Aero, Ltd., accepted the contract to supply the castings at very short notice and, in spite of having to reorganize their foundry in order to accept the additional commitments, and to obtain new moulding boxes, working day and night the 410 castings made from 15 various patterns and weighing nearly 1½ tons were delivered in four weeks. The magnesium alloy used in the castings was to specification D.T.D.59B.

The feature had a total width of more than 100 ft. and the height over the centre arch was 50 ft. Although

measuring 6 ft. × 3 ft., the largest panels, constructed of three castings, weighed only 15 lb. The whole feature was sprayed in flat white paint, the castings requiring no machining. It is interesting to note that had the original Crystal Palace been constructed in magnesium alloy, in place of wrought and cast iron, the amount of material used would have been about 1,300 tons and a saving of 3,200 tons would have been effected.

Institution of Mining and Metallurgy Awards

THE Council of the Institution announce the following:

Honorary Membership of the Institution has been conferred on SIR HENRY TIZARD, G.C.B., A.F.C., F.R.S., in recognition of his outstanding services to science, industry and education, and on SIR ANDREW BRYAN, J.P., H.M. Chief Inspector of Mines, in recognition of his distinguished services to the mining industry of the United Kingdom.

"The Consolidated Gold Fields of South Africa, Limited" Gold Medal for 1950 has been awarded conjointly to MR. J. P. NORRIE, M.I.M.M., B.Sc., and MR. W. T. PETTJOHN, for their paper on "An outline of underground operations at Mufulira Copper Mines, Ltd." (*Transactions*, vol. 59); and "The Consolidated Gold Fields of South Africa, Limited." Premium of Forty Guineas for 1950 has been awarded conjointly to MR. H. L. TALBOT, M.I.M.M., and MR. H. N. HEPKER, B.Sc., for their paper on "Investigations on the production of electrolytic cobalt from a copper cobalt flotation concentrate" (*Transactions*, vol. 59).

The "William Frecheville" Students' Prize has been awarded to MR. G. J. MORTIMER, M.B.E., A.M.I.M.M., A.R.S.M., for his paper on "Grade control" (*Transactions*, vol. 59).

The Heat Treatment of Aluminium Alloys

By J. Crowther, M.Sc., F.I.M.

Chief Metallurgist, James Booth and Co. Ltd.

Developments in the field of aviation owe much to the progress which has been made in the heat treatment of aluminium alloys. Based on Wilm's discovery that an aluminium alloy containing 4% of copper and $\frac{1}{2}$ % of magnesium hardened on standing at room temperature after quenching from 500° C., a number of alloys have been developed giving improved mechanical properties—some after precipitation at elevated temperatures—and in this article the author discusses the treatment of certain types of alloy in some detail.

It is a little over 40 years since Wilm made the famous discovery that an alloy of aluminium containing copper and magnesium hardened spontaneously, and to a very significant extent, after being quenched from a temperature of around 500° C. This discovery started two highly important metallurgical developments. One, essentially practical, commercialised the alloy and by continued improvement of the material and its logical successors made possible the modern aircraft industry; the other, more scientific, endeavoured to explain the phenomenon of "age hardening" and in the process found it to be a very common feature of alloy systems. For many years, heat treatment by solution and precipitation based on the temperature-dependent solubility of an intermetallic compound has been accepted as a standard method of improving the strength of alloys, and is a process applicable to a wider range of materials than the age-old heat treatment of steels by quenching and tempering, which is based on the allotropy of the parent metal, iron.

Precipitation Hardening

The fact that age-hardening depended on the precipitation in submicroscopic form of an intermetallic compound previously dissolved by the initial high temperature treatment was appreciated in the early 1920's, but the precise nature of the process continued to be the subject of violent argument, and is still not fully elucidated.

All this time the alloy of aluminium with about 4% of copper has remained a favourite with experimenters, thus tying theoretical and fundamental work quite closely to industrial materials. For practical purposes, what happens in this alloy is now reasonably clear. Copper is more soluble in aluminium at high temperatures than at low (Fig. 1) and in the 4% alloy is completely absorbed in the aluminium above about 500° C. The copper atoms take up positions in the aluminium crystal lattice which are similar to those occupied by aluminium atoms and are uniformly distributed throughout the alloy. On quenching in water from 500° C., this condition is retained, because of the reduced atomic mobility at the lower temperature, although the solution is now, in fact, supersaturated and unstable. The equilibrium condition towards which it tends to move is a mixture of aluminium, containing not more than about 0.3% copper in solid solution, and particles of the compound CuAl_2 which contains about 52% of copper.

On reheating somewhat, say to 100° C., increased atomic mobility allows the copper atoms to take their first steps towards separating from solution, concen-

trating in particular spots in the lattice and forming thin plates of copper-rich material along particular lattice planes. These spots can be recognised in the X-ray diffraction pattern of the material. In their

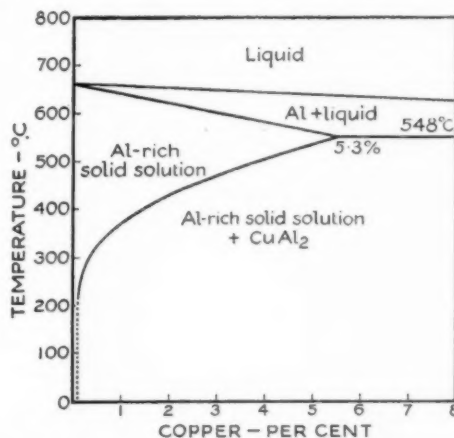


Fig. 1.—Aluminium-rich end of the aluminium-copper binary equilibrium diagram.

earliest form, the plates are too thin to take up the lattice structure of the compound CuAl_2 and remain attached to the main lattice, causing considerable strain in that lattice to accommodate the misfit. The alloy hardens progressively as these zones increase in number and size.

At a certain size, however, the copper-rich areas become capable of breaking away from the main lattice as actual particles of CuAl_2 ; a second stage of the precipitation process is, therefore, a progressive release of lattice strain with consequent softening of the alloy. Growth occurs earlier and proceeds more rapidly the higher the temperature and, at sufficiently high temperatures, ultimately produces a fully softened structure. Particles of precipitate become visible under the microscope, usually when softening is well advanced; these are at first plate-like and definitely orientated, but ultimately become rounded in the fully annealed structure. The aluminium matrix is now virtually free from strain.

As would be expected, the hardening is more intense the greater the amount of precipitate available, and is greatest in the alloy containing the maximum amount of copper in solid solution on quenching (i.e., 5.3% at 548° C.). The use of this amount of copper is, however,

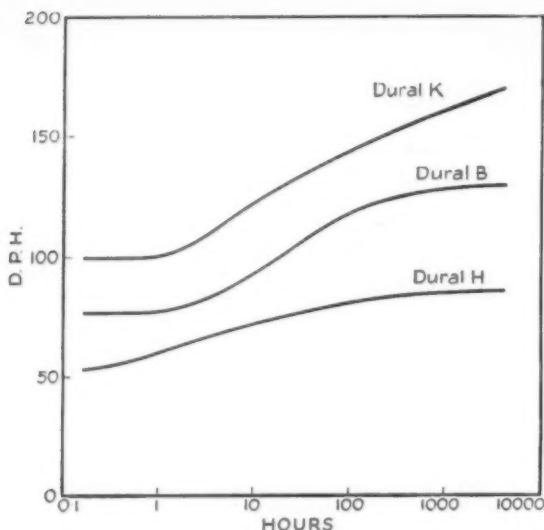


Fig. 2.—Change in hardness with time after quenching in the room-temperature ageing of three aluminium alloys.

impracticable since the temperature required for full solution (548°C.) is also the temperature at which the alloy begins to melt, and a lower copper content is necessary to permit of some latitude in solution treatment temperature (e.g., 530°C. to 560°C. at 5% Cu).

Effect of Alloy Composition

The binary aluminium-copper alloys described above produce a precipitate of CuAl_2 . Commercial wrought alloys precipitate this or other compounds according to their chemical composition and sometimes several different compounds may precipitate in the one alloy. The actual precipitation process may therefore be complex, but it is believed that it is basically similar to that described for the binary alloy.

The ordinary Duralumin, which is essentially an aluminium-copper-magnesium alloy, precipitates CuAl_2 and CuMgAl_2 , and particularly high strengths can be obtained (at the expense of ease of fabrication) by increasing the proportion of the latter compound. Precipitation takes place spontaneously over a period of many days at room temperature, the rate decreasing steadily as a stable condition is approached. There is no evidence, from very many years of observation, that room temperature ageing ever reaches the second stage of softening. The ternary compound CuMgAl_2 , although largely responsible for the hardening of Wilm's original alloy, was early confused with CuAl_2 and its separate existence was not clearly shown for some 25 years afterwards.

Compounds containing silicon are important in the modifications of the early Duralumin intended for precipitation at elevated temperatures and, in all, five precipitates, CuAl_2 , CuMgAl_2 , Mg_2Si , $\text{Cu}_3\text{AlMg}_5\text{Si}_4$ and silicon, are to be reckoned with in this general type of alloy, up to three occurring together in particular alloys.

The newest high strength alloys depend on the presence of copper, magnesium and zinc. In the absence of copper the precipitate is MgZn_2 , but when copper is present both copper and aluminium occur in the pre-

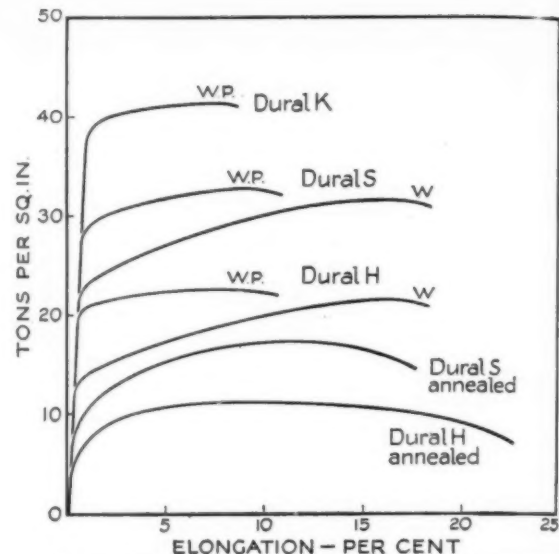


Fig. 3.—Typical stress-strain curves for three aluminium alloys after various heat treatments. (W—naturally aged; WP—aged at elevated temperature.)

cipitated compound as well as magnesium and zinc; some CuMgAl_2 may precipitate as well.

Tensile Properties

For the purpose of describing the effects of heat treatment in detail, four commercial alloys will be discussed. Typical compositions of these are given in Table I, together with a selection of relevant specifications.

TABLE I.—COMPOSITION OF TYPICAL ALUMINIUM ALLOYS.

	Cu %	Mn %	Mg %	Si %	Zn %	Cr %	BS, 1476 alloy	BS, Aircraft spec.	DTD.
Duralumin B..	4.2	0.6	0.6	—	—	—	H 14	6 L1	—
S..	4.2	0.7	0.7	0.8	—	—	H 15	—	364
H..	Nil	0.7	0.7	1.0	—	—	H 10	—	—
K..	1.0	0.3	2.7	—	5.8	0.1	(16)	—	683 363

Note.—BS, 1476 Brit. Stand. Inst. General Engineering Series.
BS, 6L1 Brit. Stand. Inst. Aircraft Material.
DTD, Ministry of Supply, Aircraft Specification.

Duralumin B is the original Duralumin, designed for good all-round properties and general utility. As normally supplied in the "naturally aged" condition, it has for very many years been subject, in a variety of forms, to the well known and easily remembered minimum specification figures:—

0.1% P.S.	U.T.S.	El%
15	25	15

Silicon is regarded as an impurity in Duralumin B but is deliberately added to Duralumin S, where it enhances the degree of response to precipitation treatments at elevated temperatures, without seriously impairing the ability to age at room temperature. Duralumin H is an alloy of somewhat lower strength, but free from copper and of greater resistance to corrosion. Duralumin K gives the highest strength practicable with aluminium base alloys.

All four alloys age to a greater or less degree at room temperature, and the change of hardness with time after quenching is given in Fig. 2. The effect is least

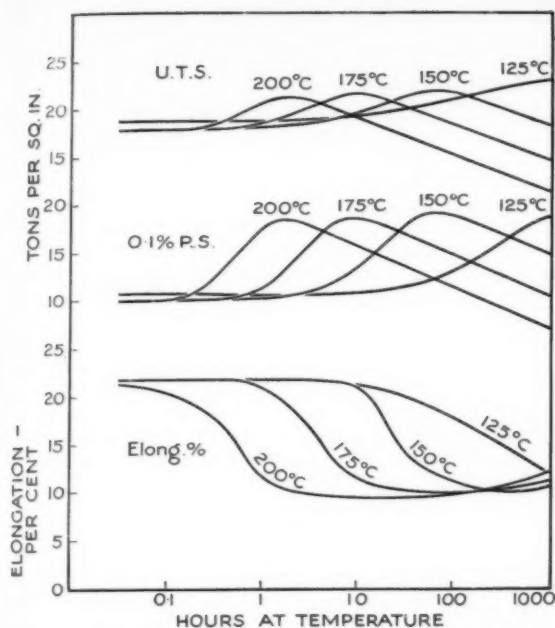


Fig. 4.—Curves showing the progress of precipitation hardening of Duralumin H at various temperatures after quenching from 525° C.

with Duralumin H but is not insignificant even with this alloy. Duralumin B, of course, depends on room temperature ageing for its properties, as normally supplied, and Duralumin S is frequently supplied in the same condition. The effect is greatest, however, in Duralumin K, Fig. 2 showing an increase of 70 in the diamond hardness of the material in 300 hours (four months); at the end of this time hardening is proceeding at a steadily decreasing rate but without clear indication of a limit. The very long time necessary to attain reasonable stability in this type of alloy is one of the reasons why it is not used in the naturally-aged condition.

Fig. 3 shows a family of typical stress-strain curves for various conditions of heat treatment in these alloys. The two naturally-aged examples given show the 0.1% proof stress to be very roughly two-thirds of the ultimate tensile strength with a long smooth work-hardening curve between the two. Precipitation treatment at elevated temperature alters the U.T.S. only slightly but increases the proof stress very markedly so that the ratio of proof stress to ultimate may exceed 0.9. This extension in the elastic portion of the curve is accompanied by a decrease in the plastic deformation possible and, in the case of Duralumin K, at any rate, the acceptable ductility level is one of the most important factors deciding the alloy composition used. Fig. 3 also contains two curves for the annealed condition in which the material is most easily worked.

The precipitation treatment may be carried out over a wide range of temperature. At any one temperature the strength first rises to a maximum and then slowly decreases. The strength-time curves for different temperatures are similar in general shape, the time to maximum strength decreasing as the temperature increases; the actual peak strength attainable is some-

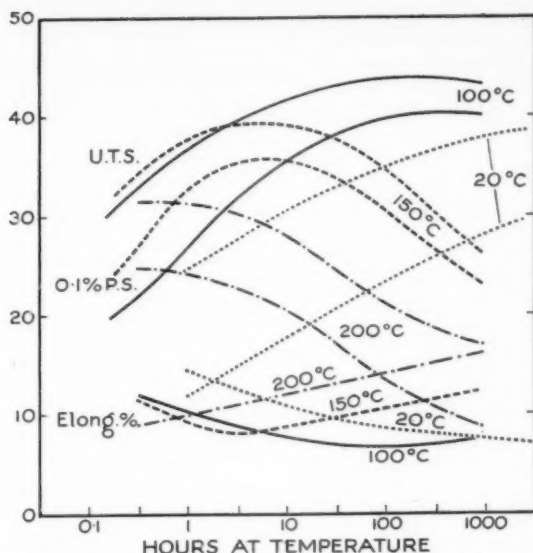


Fig. 5.—Curves showing the progress of precipitation hardening of Duralumin K at various temperatures after quenching from 460° C.

what lower at the higher temperatures. A family of such curves for Duralumin H is given in Fig. 4 and demonstrates that a treatment of one hour at 200° C. is roughly equivalent to one of a thousand hours at 125° C. Commercial precipitation is practicable in the range 200° C. to 160° C. requiring times of, say, 1 to 24 hours. The range for Duralumin S is broadly similar.

Duralumin K reacts over a somewhat different range of temperature, as shown in Fig. 5, and here the dependence of peak strength on the actual temperature used is very obvious. With this alloy the curve for room temperature ageing fits naturally into the general sequence, whereas with Duralumins B, S and H it is of quite a different nature and suggests a different set of precipitation conditions at 20° C. and 200° C. Commercial precipitation of Duralumin K uses the range 120° C. to 140° C. with times up to 24 hours. Higher strengths could obviously be obtained by precipitation at 100° C. but much longer times would be required; the proof-stress: ultimate-strength ratio would probably be higher and the elongation at fracture lower. Fig 5 shows quite clearly how the P.S.: U.T.S. ratio varies with precipitation temperature, although the relatively low ratio for the portion of the natural ageing curve shown may be modified in several years' ageing.

The curves reproduced refer to material in forms most suitable for use in the laboratory, e.g., 1 in. diameter extruded bar. They illustrate adequately the general behaviour of the alloys, but the actual level of strength attained will naturally vary with the form and size of the particular product considered.

Solution Treatment

The function of solution treatment is simple—to convert the alloy into a uniform solid solution for subsequent precipitation hardening. The main requirement is adequate time for maximum solution of the available soluble constituents, although in practice the time may be curtailed for secondary reasons, such as restriction of grain growth.

There is an optimum temperature for solution treatment; if the temperature used is too low, the actual solubility may be restricted and the final mechanical strength impaired; if too high, then the solidus temperature may be exceeded and the metal damaged by partial liquation. Duralumin B has a wide tolerance of solution treatment temperature and, although the nominal figure is about 490° C. in many forms temperatures from 475° C. to at least 505° C. are permissible metallurgically if not by the letter of a specification. Duralumin S is an example of an alloy designed for the limit of strength possible from that particular combination of elements by having rather more constituent than will dissolve at the melting temperature of the lowest eutectic, the highest temperature that may be used in solution treatment without causing liquation. Any practicable treatment must use a temperature somewhat lower than this, with consequent decrease in the solubility of the alloying elements and lower final strength. A particular instance of the dependence of properties on quenching temperature is given in Fig. 6, which indicates why close control is necessary in the treatment of this alloy.

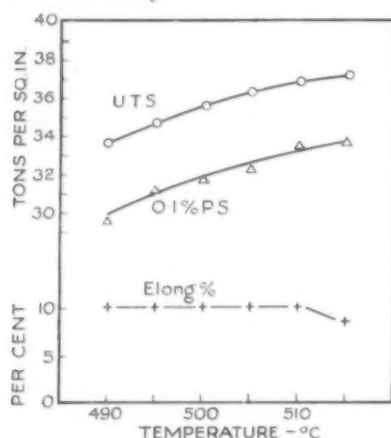


Fig. 6.—Effect of quenching temperature on the tensile properties of Duralumin S subsequently precipitated 4 hours at 185° C.

It has been demonstrated that in this type of alloy the actual solidus temperature varies very significantly from 509° C. to 515° C., or higher, with relatively small changes in composition (particularly the magnesium and silicon contents), with consequent reaction on the maximum solution treatment temperature possible without a certain amount of grain boundary liquation. Although the practical importance of small amounts of liquation can be over-rated, it does increase any tendency to crack on quenching.

Duralumin K presents a much easier case. Its composition is determined by the level of ductility which must be retained after heat treatment, and in this alloy system full saturation with copper, magnesium and zinc is not desirable. Although adequate solution is obtained at 460° C. the solidus of well homogenised wrought material is over 520° C. Hot working temperatures are quite close to solution treatment temperatures (there being no danger of overheating) and produce considerable refinement of the soluble constituents so that, if the final product is well wrought,

solution treatment is a very rapid process. As a corollary to this, of course, material fairly rapidly cooled after hot working, or even the original cast billet, can age harden very markedly.

In any alloy, the actual time required for solution treatment varies with the coarseness of the structure; sheet may take only 1 to 2 minutes, relatively unwrought material several hours. Similarly, the actual solidus temperature may vary with the degree of homogenisation since casting. As mentioned above, Duralumin K may safely be heated to 520° C. when well wrought, but in the cast material eutectics down to 476° C. are present.

A well known phenomenon in the heat treatment of steel is "mass effect," the critical dependence of hardening on cooling rate which is shown up by the refusal of bars above a certain size to harden throughout. Until recent years this effect was not significant in aluminium alloys, lower core properties being rather a function of coarser structure, but in Duralumin K type alloys it can be demonstrated that mass effect is a factor in the difference in properties observed between skin and core of large extrusions.

Annealing

The softening of the strong aluminium alloys by annealing may involve one or both of two quite different processes. As noted above, the second stage of the precipitation process leads to softening and, in Duralumins B, S and H, heating of precipitation-hardened material to about 350° C. to 400° C. produces rapid coarsening of the precipitate to give a stable soft alloy. The precipitation curves for Duralumin H given in Fig. 4 show that very long treatments at lower temperatures may produce considerable softening, a thousand hours at 200° C. having the same sort of effect as a few minutes at 300° C. At temperatures above about 350° C. solution-treatment effects begin to complicate the issue: a small amount of alloying constituent dissolves during the annealing treatment, is retained in solution during cooling and subsequently precipitates on standing to cause noticeable age-hardening. The commercial treatment, therefore, adopts a compromise temperature which, while causing softening in an acceptably short time, does not allow serious age-hardening in the annealed material. In line with the lower temperatures used for solution and precipitation treatments in Duralumin K, the temperature for stable annealing is also somewhat lower at about 300° C.

The second process in annealing is the recrystallisation of a cold worked material, which for simplicity we can assume to be stably soft as far as precipitation effects are concerned. Such a case occurs, for example, in interstage annealing during sheet rolling. At the temperatures needed for the "over-precipitation annealing" previously discussed, this recrystallisation of sufficiently cold worked material takes place in a few seconds.

Stress-strain curves of annealed Duralumins H and S are to be found in Fig. 3.

Industrial Heat Treatment

The industrial heat treatment of the strong aluminium alloys demands, above all else, precision of temperature control, if the material is to comply consistently with aircraft specifications. The solution treatment temperature permissible is fixed by such specifications to a

narrow range, usually $\pm 5^{\circ}\text{C.}$, about the nominal figure, although for general purposes a less rigid control can often be allowed. In the case of furnaces designed for treating large extrusions and forgings, temperatures must be maintained well within this range throughout a chamber which may be 40 ft. \times 3 ft. \times 2 ft. At the temperatures concerned, radiation can play little part in heat transfer and so the standard type of furnace relies on a forced circulation of air. Taking an electrically heated furnace as an example, air is directed by fans over a bank of resistance elements and then over the furnace charge which is screened from direct radiation from the elements. There may be a single stream directed axially along the whole furnace length or several fans in the furnace roof may give a mainly transverse flow. Temperature control is by thermocouples placed at carefully selected positions in the moving air stream, and large furnaces may be controlled quite independently in two or more sections for better uniformity. The maintenance of constant temperatures and their accurate measurement throughout the furnace calls for adequate instrumentation and considerable experience in pyrometry.

As stated previously, the main requirement of solution treatment is simple—that the charge shall be heated to the required temperature for a long enough period to cause adequate solution of the hardening elements. In practice, as so often happens, the time used is a compromise, determined by a number of metallurgical and economic factors, some of them mutually incompatible. Metallurgically, the benefit to strength of a long soak at temperature must be balanced against the increased tendency to defects such as coarse grain size and blisters due to gas pick-up in the furnace. For uniformity of conditions between inner and outer members of a charge, the heating rate must be slow, or the charge small, if the inner is not to lag seriously behind the outer; slow heating favours coarse grain, while small charges lead to inefficient use of the furnace if the length of soak at temperature is not negligible compared with the heating time. The actual conditions used may therefore vary considerably from load to load according to which factor becomes of primary importance.

Conditions of quenching may also vary. For highest strength in bulky forgings or extrusions, the quickest possible quench is desirable. This, however, produces maximum temperature gradients in the metal with consequent high internal stress. In a short thick body this may not matter very much since the surface is usually under compressive stresses, but subsequent machining may unbalance the stressing and cause distortion or bring tensile stresses to a free surface where they may prejudice service life. When one dimension is very dissimilar to the others, as in an extrusion, distortion always occurs; this may be corrected by local bending or twisting, but a non-uniform stress system is left which may give rise to serious distortion on machining. An adequate amount of controlled longitudinal stretching, however, is capable of removing the undesirable stress system almost completely. All such rectification should be done as soon as possible after quenching, before the metal begins to age appreciably, as work done later requires higher forces and deformations and leaves higher residual stresses.

Serious distortion may result where sudden changes of thickness occur in forgings or extrusions, and may

lead to cracking. It may be minimised by controlling the way in which the body enters the water or by using a less drastic quench—into hot water or oil, for example.

Precipitation treatment demands accurate control of both temperature and time. The load must be heated as uniformly as possible if all parts are to have the same effective time at precipitation temperature and, since some precipitation occurs during the later stages of heating up, the optimum time at temperature depends somewhat on the rate of heating and hence on the size of load. General practice aims at using the time giving peak strength for a given temperature, and for this time reference to Fig. 4 shows that a variation in time of about $\pm 30\%$ is not very important. This tolerance does not apply if one is aiming at a point on the rising portion of the curve. Many alloys may be given approximately the same properties by a short-time at the upper end of the permissible temperature range or by a much longer time at the lower end, and greater throughput may be achieved at the higher temperatures. Somewhat better control of properties and of uniformity throughout a furnace charge may, however, be expected at the lower temperatures, since heating up time will then be a much smaller fraction of the total time and its effect on the difference in soaking time of various parts of the charge will therefore be less.

Aid to Air Freight Shippers

BECAUSE of intense competition for overseas markets more and more manufacturers and shippers are using air transport to meet their customer's demands. Although documentation and export procedure are much simpler for air transport it was felt by B.O.A.C. that a book of reference would be a boon to the shipper when despatching his consignments and a B.O.A.C. series of "Air Freight Booklets" was therefore produced. Issue No. 1 was published in February, 1947, and contained 14 small pages, but with the introduction of more and more facilities, further space was required and the present issue contains 20 large pages full of essential information.

In the booklet are details of all the Corporation's numerous facilities for the carriage of air freight from the U.K., including special collection services, favourable insurance rates and special commodity rates for certain classes of goods. Information is also given about such varied subjects as C.O.D., Charges Forward, Export Documents and the maximum size of packages which can be accommodated in each type of aircraft flown by B.O.A.C.

As B.O.A.C. has one of the world's largest networks of air routes, rates can be quoted to almost every point of major importance. Air freight charges to over 350 of these points are listed in alphabetical order in the booklet and should cover the needs of shippers in most instances. The foregoing is only a sample of the varied information provided; anyone interested in the despatch of air freight to anywhere in the world should ask any B.O.A.C. appointed forwarding agent, or any Corporation Office for a copy of the publication.

On May 1st, 1951, the name of Mullard Electronic Products, Ltd. was changed to "MULLARD, LTD." The Company's products are being distributed throughout the world on an ever-increasing scale and the new name has been adopted in order to associate the Company more closely with its Trade Mark "MULLARD."

Correspondence

Tensile Failure of Carbon and Stainless Steel Wires in the presence of Water and Hydrogen Sulphide

The Editor, METALLURGIA.

Sir,

The January, 1951 issue of METALLURGIA has just reached here, and I was interested in the contribution by Mr. J. E. Truman on "Tensile Failure of Carbon and Stainless Steel Wires in the Presence of Water and Hydrogen Sulphide," since I was associated with a similar investigation at one time.

Mr. Truman states that he found no branching cracks of the type usually present with stress corrosion, and it would be of interest to know the criterion he used in assessing this; the experience of the present writer, when working at N.P.L., Teddington, on the stress corrosion of an alloy steel under similar conditions¹ was that it was often necessary to select areas for microscopic examination with great care, as cracking could be very local and not necessarily near the point of fracture. It was found that use of a magnetic crack detector with a specially developed technique permitted a verdict of "not cracked" to be given with certainty, and made possible the pre-selection of cracked areas for examination in the polished section.

The fact that Mr. Truman was unable to reproduce cracking and a rapid failure such as that cited by Rees² can probably be explained by a consideration of the effect of the concentration of water vapour. In the tests cited above¹ it was found that the presence of hydrogen sulphide that was merely moist did not produce cracking or greatly accelerated failures, but that the gas had to be fully saturated with water to do so, although it was not certain that actual deposition of "dew" was necessary to initiate stress-corrosion. It is significant, however, that heavy corrosion and accelerated failure were produced when the surfaces of specimens were kept wet by a wick dipping in water. It seems likely, therefore, that small differences of experimental conditions could easily influence the local concentration of water vapour or droplets and control the onset of cracking. It is also worth noting that most of the tests at N.P.L. were conducted by uniform bending, which might be expected to produce more areas containing cracks than a straight tensile test as used in the work in the Firth-Brown Laboratories.

Both the reports deal with the solution of a technical problem concerned with the use and value of certain steels under certain conditions, but there is obviously scope for further detailed and systematic investigation of the phenomenon.

Yours faithfully,

R. C. GIFFKINS.

Commonwealth Scientific and Industrial Research Organisation—Physical Metallurgy Section,
The Baillieu Laboratory, University of Melbourne,
N.3, Victoria, Australia.
March 28th, 1951.

¹ "Stress-Corrosion Cracking in Alloy Steel Gas Cylinders," R. C. Giffkins and W. P. Rees, *Metal Treatment*, Autumn, 1948, XV No. 55, p. 109.

² Note on Stress Corrosion Cracking of Steels in the Presence of Sulphur Compounds. W. P. Rees, Inst. of Metals Symposium on Internal Stresses in Metals, 1947.

The Editor, METALLURGIA.

Sir,

I have read with interest the copy of the letter dated March 28th, from Mr. R. C. Giffkins, regarding my article "Tensile Failure of Carbon and Stainless Steel Wires in the Presence of Water and Hydrogen Sulphide," and I would offer the following comments on the various points raised by Mr. Giffkins.

Magnetic crack detection was not used to assess the presence or absence of cracking. It would in any case be difficult to apply such a method to the wire samples used and it could not be used at all for the practically non-magnetic 18/8 steel. All the test samples were carefully examined at high magnification, however, and no branched cracking could be detected. In fact, no relationship of the corrosion or fractures to structure could be found, but there was considerable loss of ductility as evidenced by the absence of necking at the fractures as compared with the fractures of similar specimens tested in tap water without hydrogen sulphide.

The difference between the time to failure of 18/8 steel wire in the present tests and in those reported by Rees can hardly be explained by lower concentration of water vapour in our tests, as the wires were partially immersed in water held in the enclosing tubes and through which the hydrogen sulphide was slowly bubbled. It is interesting to note that fracture did not always take place at the same point, but in different tests occurred above the water level, at the water level, below the water level and also in the lower wax seal. A possible alternative explanation lies in the different conditions of the steels used in the two sets of tests. The material used by Rees was 0.02 in. diameter hard drawn wire, which contained a great deal of internal stress. It required a load of 80 lb. to break it, corresponding to a maximum stress of 113 tons/sq. in., as opposed to the value of 66 tons/sq. in. for the 18/8 steel wire used for the present tests. Thus the actual load per square inch applied to the test pieces in each case was quite different. It is of interest to note that agreement was closer in the case of the carbon steel wires, where material of similar condition was used for both series of tests.

Yours faithfully,

J. E. TRUMAN.

The Brown-Firth Research Laboratories,
Sheffield.
May 11th, 1951.

British Aluminium Buses for U.S. Air Force Personnel in Great Britain

THE United States Government has ordered 10 British aluminium passenger observation coaches (similar to that which won the Grand Prix at Nice last year) and 55 British aluminium ordinary passenger coaches for the use of Air Force personnel in Great Britain. The total order amounts to 200,000 dollars—which is of course, an export without any goods leaving Britain. The coachbuilders are Messrs. James Whittit & Co., Ltd., of West Drayton, Middlesex. The observation coaches are mounted on Crossley Diesel engine chassis and are 30 ft. long, the ordinary coaches on Austin Loadstar chassis and are 29 ft. long. The first two of each were handed over by the builders to Col. Riggs—Deputy Chief of Staff of the U.S. Air Force in Great Britain, at Ruislip on Saturday, April 14th.

The Work of the Welding Engineer

By P. L. Pocock, A.M.Inst.W.

Recent years have seen a more scientific approach to the application of welding in engineering production. Whilst it still continues to give excellent service in the repair shop, modern production trends have raised welding to the status of an engineering process comparable in importance with forging, casting and machining. This advance has been accompanied by a demand for engineers experienced in the application of the various welding processes to engineering construction; the author draws attention to a few aspects of the work of the welding engineer.

DURING the past ten years, the volume of welding employed in plate fabrication and other spheres of engineering has been continuously on the increase, and this advance in the use of welding has brought about a demand for fully experienced welding engineers. To achieve and stabilise a high standard of welding, and to establish a sound basis for production economy, the scope and responsibility of the welding engineer in a well-organised concern is very great, and his duties should include acting in an advisory capacity in designing, estimating and planning for welding, and directing the technical and scientific development of welding generally.

The competent welding engineer should be conversant with all the widely used processes of welding, possess a good general engineering knowledge, together with specialist training in metallurgy, the design of jigs and fixtures and the design of welded structures. It is also desirable that he should have a working knowledge of radiography.

The organisation and layout required to obtain maximum efficiency in welding production does not differ greatly from that required in other branches of engineering, but although an efficient company would not consider laying out an engineering shop without the necessary jigs and fixtures for economical production, it has been the practice in the past, and still is in many instances, for welding to be carried out haphazardly in any odd corner and with machines and plant completely inadequate for the work in hand.

When one has to consider fabricated platework, such as the diesel engine housing and L.P. turbine casing, shown in Figs. 1 and 2, the sub-assembly method of construction is the only logical process by which this class of work can be produced. Allowances must be made for distortion and the use of pre-machined parts, and planning for this class of work is a specialist job which can only be effectively carried out by engineers with an intimate knowledge of welding problems.

It is essential for all operations in the welding shop to be carefully considered in every detail to ensure a high standard of welding, each factor affecting this being rigidly controlled. The planning must be practical and efficient to include allowances for all contingencies, and must specify: (a) the type and gauge of electrodes to be used, (b) method or process of welding, (c) amperage for



Fig. 1.—Diesel engine housing.

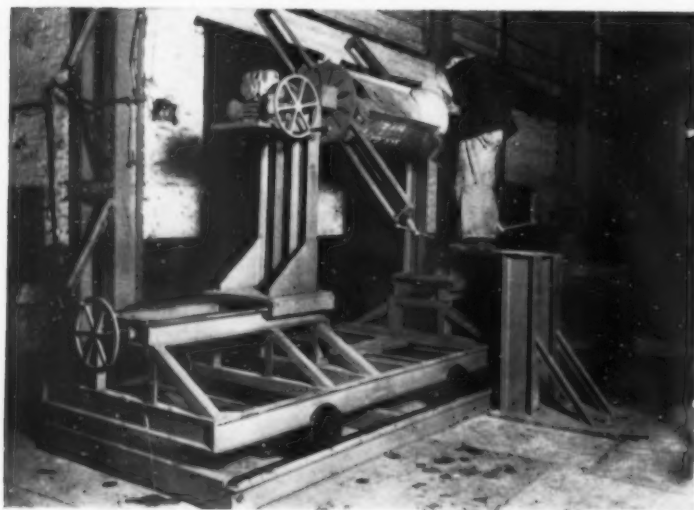
each run of weld metal deposited, and (d) the joint preparation.

Net Arc Burning Time

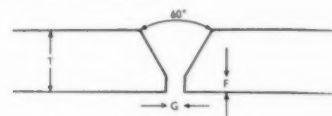
Piece-work systems if mutually agreed between management and welders can be very effective in maintaining production and minimising costs, so long as they are based on average ability and the more efficient welders obtain the benefit of their performance. This also acts as an incentive to other welders in the shops. However, the yardstick by which production is planned and the basis of piece-work times must obviously be the net arc burning time, i.e., the actual time the arc is burning to deposit a given volume of weld metal, together with an allowance for handling and de-slagging, plus an operational fatigue allowance. This can be summarised as follows:—

Net Arc Burning Time + Handling + De-slagging + Fatigue Allowance = Output Man Hours.

For production piece-work times to be too high retards production in just the same way as do times which are far too low. To ensure that the rate fixers set correct and equitable times, they should have to hand detailed information to guide them; this can only be done if welded joints are standardised wherever possible and charts made up giving the volume of metal required



for each type of joint, and the net arc burning times for a given volume of weld metal for each gauge of electrode. To determine the quantity of weld metal required for a given size of joint, the formula below can be used but it is always advisable, especially in the case of a square-edge butt joint, to carry out tests to ascertain the correct volume of weld metal required, and the information should be recorded.



Sketch A

Example :—To obtain the quantity of weld metal required per foot of joint, as shown in Sketch A, take the following formula (in which $A = \tan 30^\circ = 0.5774$):

$$12 [(T \cdot F)^2 A + GT]$$

and add 10% to the total metal required, for weld reinforcement.

There are several factors which affect the arc burning time and these can be roughly classified as follows:—

1. Type of electrode.
2. Position of weld (use of manipulators, jigs and fixtures).

In determining the net arc burning time, the type and make of electrode must be considered, since there are variations in the deposition rate and the amount of metal deposited. This information is again best compiled from practical tests; most electrodes are in general only 80% efficient taking into consideration losses due to stub ends, splatters, etc. However, the usual method of determining the efficiency is carried out as follows:—The weight of the test plate is taken before welding after being thoroughly cleaned, again after welding when slag and splatter have been removed; this difference in weight is then compared with the amount of electrode used which is calculated by weight before and after welding.

The position of the weld is a deciding factor in the fixing of times since the volume of weld metal which may be deposited in a given time in H.V. fillets, overhead and vertical joints, varies with the position of joints. Manipulators and jigs and fixtures should be used wherever possible to position the joint for down-hand welding.

Manipulators

Manipulators or jigs can be designed and installed for almost all types of fabri-

Fig. 2. (top).—L.P. turbine casing. Fig. 3 (middle).—Rotary manipulator for vessels and pipework. Fig. 4 (bottom).—Manipulator similar to that shown in Fig. 3, but designed for more general platework.

eration ranging from 1 ton to 50 tons or more in weight. The main advantages arising from their use are: (a) the reduction of fatigue (and, therefore, of production costs), (b) saving of floor space, and (c) improvement of welding quality. Manipulators can be classified under two distinct types:

- (A) Manipulators designed to position all joints in the down-hand position, thereby making the welding operations as simple as possible.
- (B) As in (A) but also designed so that the speed of welding can be predetermined.

Illustrated in Fig. 3 is a rotary manipulator for vessels and pipework. With this type the operators stand on a platform and weld whilst the job is rotated. Investigation has proved that handling time can be reduced by approximately 20%. It should always be the aim to use the largest size electrode practicable, since apart from the marked effect on welding economy it is beneficial to weld quality and, with the aid of this type of manipulator, larger electrodes are used and the speed of rotation set to give the required size of weld.

A similar manipulator is shown in Fig. 4, but it is designed for a more general type of platework. The work is suspended and rotated between the two pillars to bring each joint into position for welding. The whole jig is then driven by a variable-speed motor and welding is carried out at a set speed whilst the welding seam moves under the operator's arc.

Handling time varies with the type of production, layout of shops and other factors peculiar to each organisation, but can be scientifically investigated to ensure that times are adequate and fair and that production time is not wasted.

De-slagging time varies with the type and size of joints, but can quite easily be tabulated. Due to the high currents necessary with large electrodes, their use is accompanied by an increase in fatigue. The following percentages can be taken as a rough guide:—

$\frac{1}{4}$ in. Electrodes	2%
$\frac{5}{16}$ in. "	7%
$\frac{3}{8}$ in. "	10%
Vertical Welding	10%
Overhead Welding	15%

Distortion

Distortion is another factor which must

Figs. 6 and 7, showing equipment fabricated for Messrs. Foster Wheeler, Ltd., are reproduced by courtesy of the Anglo-Iranian Oil Co.

Fig. 5 (top).—The "Fusarc" type automatic welding of a self-supporting chimney base. Fig. 6 (middle).—Precipitator inlet flues. Fig. 7 (bottom).—Precipitator hopper sections.

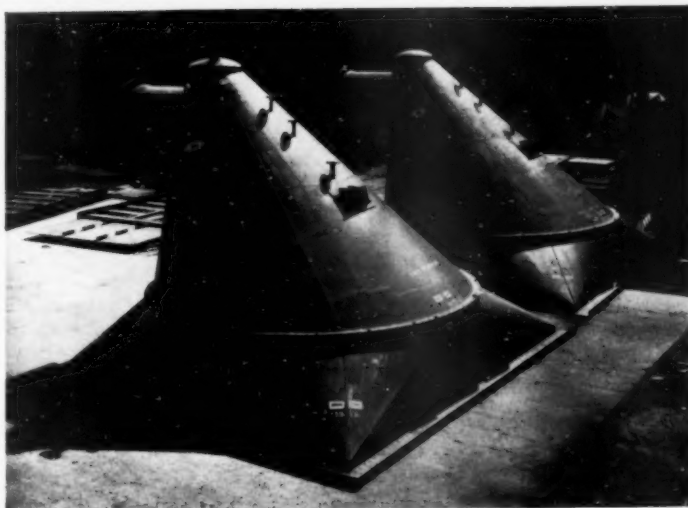
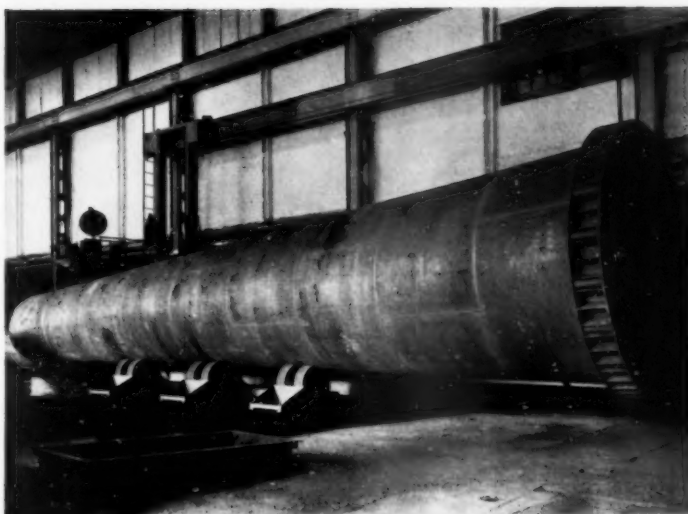




Fig. 8.—Gamma-ray testing of fabricated oil pipes.

be taken care of, since it can be a contributory cause of high production costs in welded work. Investigation has proved, although the fact is not generally accepted, that the larger the electrode used on a given size of welding joint the less attendant distortion. To give an example of this, instead of using 6 s.w.g. electrodes for butt welding $\frac{3}{8}$ in. plate, $\frac{5}{16}$ in. electrodes should be used and the welding travel speed increased. This results in a reduction of the heat-affected area on the parent metal due to the speed increase, and a corresponding reduction of distortion. This method of welding is also effective in increasing the depth of penetration. It is relatively easy to make up information tables for distortion problems, and in many cases allowances can be made for it at no resultant increase in cost.

Shop Layout and Welding Quality Methods

Shop layout is one of the most important factors in achieving production economy, layout being arranged so that the work flows smoothly from one operation to another without bottlenecks.

The welding engineer should always be alive to the possibility of adopting new methods of welding production. There are several processes such as "Fire-cracker Welding" and hand electrode semi-automatic methods which can be adopted for the welding of small assemblies of a similar type in reasonable quantities.

When the class of work warrants it, automatic welding should be employed since the increase in footage welded per hour is considerable, resulting in saving in production costs.

The "Fusarc" type automatic welding of a self-supporting chimney base is illustrated in Fig. 5. This machine is capable of welding circumferential seams in vessels 14 ft. in diameter, and longitudinal seams 40 ft. long. The welding speeds vary, with plate thickness, from 12 to 36 in. min.

Maintaining a high standard of welding does not solely depend on close supervision and inspection of welding alone. One of the largest contributors to high

costs and bad welding is bad preparation and fit up for welding. The welding engineer should ensure that all preparations for welding are carried out correctly and in accordance with the planning schedules. Examples of fabricated platework are illustrated in Figs. 6 and 7. These have been carefully assembled and prepared for welding, resulting in first-class jobs.

It is also necessary to ensure that welding personnel are regularly tested, and that their workmanship is of the required standards, records being kept giving the details of all tests, in order that welders may be employed on the various classes of work to which they are best suited, apart from tests called for by customers or other inspection organisations. Random tests should also be carried out on work in the course of fabrication.

An excellent method for spot checking of work in production is the gamma-ray process, although with this method, due to the radio-active nature of the isotopes employed, sufficient space must be available on the shop floor to comply with safety regulations. If this is not possible, the plant should be used between shifts whilst the shops are relatively clear of operators.

Acknowledgments

In conclusion the author wishes to thank the Directors of the Redheugh Iron and Steel Co. (1936), Ltd., for the use of illustrations and for permission to publish the foregoing information.

David Brown (Canada) Ltd.

THE David Brown Corporation, Ltd., formed in March, announces the establishment in Canada of a new company, David Brown (Canada) Ltd. Formation of this new enterprise, which will be based on Toronto, is primarily intended to supplement the existing agency coverage of the Corporation's gear-manufacturing group, headed by the parent company, David Brown & Sons (Huddersfield) Ltd. Initially the new branch will act as a sales organisation covering Eastern Canada on behalf of this group. Representation in Western Canada will continue to be handled by Gordon Russell, Ltd., of Vancouver, B.C., whose connection as agents for David Brown machine-cut gears extends over many years. Another established agency connection which remains unaltered is that of A. C. Wickman (Canada) Ltd., of Toronto who will continue to handle the wide range of David Brown gear and spline hobbing machines built by David Brown Machine Tools, Ltd., Manchester, and precision tools made by The David Brown Tool Company, Huddersfield.

Initial objective will be to step up the sales in Canada of a well-known David Brown product, the Radicon Worm Reducer, which is already in wide use in Britain and overseas. Designed and manufactured by David Brown & Sons (Huddersfield) Ltd., and also by David Brown Gears (London) Ltd., these versatile gear units are supplied in a comprehensive series of standard sizes ranging from 1½ to 28 in. centres and are capable of innumerable applications in almost every branch of industry. Large stocks of these units of sizes up to 12 in. centres and with an extensive selection of ratios will be made available to the new Toronto organisation. Units in the larger sizes will be shipped as required from the United Kingdom manufacturers, who also intend to include a selection of Radicons on their stand at the forthcoming Canadian International Trade Fair.

NEWS AND ANNOUNCEMENTS

The Iron and Steel Institute Bessemer Medal

As previously announced, the Council of The Iron and Steel Institute have awarded the Bessemer Medal for 1951 to Mr. Benjamin Fairless, President of the United States Steel Corporation, in recognition of his distinguished services to the iron and steel industry. As Mr. Fairless could not attend the Institute's annual general meeting in London, Sir Charles Goodeve, O.B.E., D.Sc., F.R.S., Director of the British Iron and Steel Research Association and leader of the Anglo-American Iron and Steel Productivity Team now visiting the United States, presented the Medal to Mr. Fairless during the annual general meeting of the American Iron and Steel Institute in New York on May 24th, 1951.

Institution of Mining and Metallurgy Symposium on Mineral Dressing, September, 1952

ARRANGEMENTS are now being made by the Council of the Institution of Mining and Metallurgy to hold a two-day Symposium on Mineral Dressing on September 23rd and 24th, 1952, at the Imperial College of Science and Technology, South Kensington, London, S.W.7. The purpose of the Symposium will be to discuss recent developments: (a) in fundamental concepts and experimental methods; (b) in practice at selected plants of particular interest; and (c) in plant design and machine manufacture.

Several papers are already in preparation, and others are being considered by prospective authors. Anyone who wishes to submit a paper is invited to send a synopsis of its contents and an indication of its probable length to the Secretary of the Institution, Salisbury House, London, E.C.2. All papers accepted for the Symposium will be sent as preprints to those who propose to attend the two-day discussion, and a volume containing the papers and a report of the discussion will be published after the meeting.

Further particulars will be announced later.

A Central Index of Translations

In order to assist industrialists and scientific research workers to keep themselves informed of developments in research in foreign countries the Association of Special Libraries and Information Bureaux is preparing a central index of translations. The index will include scientific papers, reports and published articles which appear in foreign journals. Work on the index has already commenced and it is intended that when complete it will provide a guide to all translations held in this country and the Commonwealth. The usefulness of the index will depend on its comprehensiveness and to make this as wide as possible the co-operation of organisations at present in possession of translations is sought. All organisations holding translations and willing to take part in the scheme are invited to get in touch with A.S.L.I.B.

A limited number of translations has already been indexed and enquiries concerning the existence or

location of translations are being dealt with. Enquiries can be made by telephone, letter or personal call. The name of the author or of the journal in which the paper sought for appeared should be quoted. There is no charge for the use of the index service.

All enquiries, and all offers of co-operation in the preparing of the index should be made to A.S.L.I.B., 4, Palace Gate, London, W.8. (Tel. WESTern 6321-3).

The Institute of Metals Oxford Local Section

At a well-attended meeting held in Oxford on April 17th, 1951, it was resolved to request the Council of the Institute of Metals to approve the formation of an Oxford Local Section, to serve a wide area around that city. The President, Chairman of the Local Section Committee and Secretary of the Institute were present. The meeting was opened by Dr. W. Hume-Rothery, O.B.E., F.R.S. The request to form an Oxford Local Section has been welcomed and approved by the Council.

The following officers of the Section have been elected for the session 1951-52:

Chairman: DR. H. M. FINNISTON.

Vice-Chairmen: DR. W. HUME-ROTHERY, F.R.S., and DR. R. T. PARKER.

Honorary Secretary: DR. B. R. T. FROST.

Honorary Treasurer: MR. J. C. ARROWSMITH.

Members of Committee: MR. H. CHADWICK, DR. J. CHRISTIAN, MR. G. MURRAY, MR. A. A. PEARSON, DR. A. E. W. SMITH, MR. D. SUMMERS-SMITH, and DR. J. THEWLIS.

Members and non-members of the Institute who wish to enrol as members of the Local Section, or who wish for further particulars, are requested to apply to the Honorary Secretary of the Oxford Local Section, Dr. B. R. T. Frost, Atomic Energy Research Establishment, Harwell, Didcot, Berks.

B.O.C. Prize for Welding Research

THE Council of the British Welding Research Association gratefully accepted an offer from the British Oxygen Co., Ltd. in 1948 to provide a prize fund for a competition relating to welding for three years. The first competition was held during 1948/49 when no award was made. In 1949/50 a prize was awarded to K. Winterton, Ph.D., C. L. M. Cottrell, M.Sc., and J. G. Ball, B.Sc., A.I.M. for their paper entitled, "A New Weldability Test for Magnesium Alloy Sheet." The result for 1950/51 has not yet been arrived at, the papers still being in the hands of the assessors.

As no award was made during 1948/49 a single prize of £100 is offered again this year and will be awarded for the best paper submitted on a research into welding or its applications. The competition is limited to candidates whose age did not exceed 35 years on January 1st, 1951. Papers submitted for the competition must reach the Secretary, British Welding Research Association, 29, Park Crescent, London, W.1 (from whom further particulars may be obtained) on or before December 31st, 1951.

The Aluminium Development Association

Annual General Meeting

THE annual general meeting of The Aluminium Development Association was held on April 20th, 1951, when Mr. Austyn Reynolds, B.A., A.M.I.Mech.E., A.F.R.Ae.S., was elected President for the year 1951/52. Mr. Reynolds is, of course, a director of Tube Investments, Ltd. and Deputy Chairman of T.I. Aluminium, Ltd. and the associated Aluminium Companies. He has served on the A.D.A. Council for six years and was Vice-President of the Association during 1950/51. The new Vice-President is Mr. H. G. Herrington (High Duty Alloys, Ltd.). Mr. F. G. Woollard, M.B.E., M.I.Mech.E., M.I.P.E., M.S.A.E., was re-elected Chairman of the Executive Committee.

At the meeting, the retiring President, Mr. Edward Player, introduced the annual report of the Association by drawing particular attention to those activities linked with long term development of aluminium in the major engineering industries.

Enlarged London Laboratories for B.I.S.R.A.

THE British Iron and Steel Research Association announce that they have acquired the whole of the light industrial premises at 140, Battersea Park Road, London, of which their Physics, Chemistry and Plant Engineering laboratories now occupy about one-quarter. This will make available some 43,000 sq. ft. of additional laboratory and office accommodation, until recently occupied by the research department of Powell, Duffryn Research Laboratories, Ltd. The Association's Plant Engineering Division and Chemistry Department, including the Corrosion and Refractories Sections, will move into the new accommodation as soon as necessary alterations have been sufficiently completed. Starting within the next two months the move will be probably completed in the autumn of this year. This in turn will make possible an expansion of the Physics Laboratories.

Swedish Ore Concentration Works

A NEW ore-concentration works, reported to be one of the largest and most modern in Europe, is at present being built by the Boliden Mining Company in North Sweden. Built in two sections, the new works will have a total annual capacity of 1,000,000 tons when completed early in 1954.

New Tin Research Laboratories

THE DUKE OF GLOUCESTER will open the new Laboratories of the Tin Research Institute at Greenford on Thursday afternoon, May 31st. Diplomatic representatives of tin-producing and consuming countries and many distinguished scientists and industrialists will be present. On Friday, June 1st, the Laboratories will be open all day for inspection.

One Hundred Years of Aluminium

As a small contribution to the Festival of Britain, The Aluminium Development Association has arranged a special miniature exhibition to illustrate the phenomenal growth of aluminium from a chemical curiosity in 1851 to a metal of primary industrial importance to-day. The predominating part played by aluminium in the South

Bank Exhibition makes it appropriate to show the important part played by Great Britain in the development of the Aluminium Industry throughout the world.

The Exhibition, which was opened by the President of the Association, Mr. Austyn Reynolds, on Thursday, May 10th, 1951, will remain open until September 28th, 1951 (Mondays to Fridays from 9 a.m. to 6 p.m.). It symbolises the growth of an industry: beginning with the discoverer who first believed in the potentialities of aluminium, it illustrates development to its modern stature. The earliest exhibits typify the small successes of the industry's pioneers, and contrast vividly with the scope and magnitude of present day applications.

Personal News

H.R.H. THE DUKE OF EDINBURGH, K.G., has been admitted into the Fellowship of the Royal Society.

MR. O. W. HUMPHREYS has been appointed Director of the Research Laboratories of the General Electric Co., Ltd. For the past two years, Mr. Humphreys has been the Manager of the Laboratories, having been appointed to that position following the death of Sir Clifford Paterson.

MR. IDRIS WILLIAMS, Assistant Manager of the Continuous Pickling and Hot Sheet Finishing Departments at Ebbw Vale, has been appointed Assistant to the Plant Manager at the Trostre Works of the Steel Company of Wales, Ltd., and will cover the Pickling Department, Cold Reduction Mill, Cleaning Lines and Annealing Departments.

National Research Corporation announces that MR. G. KIDDOO has been appointed Assistant Director of its Petrochemical Research Department.

DR. C. F. BAREFORD, Head of the Mullard Electrical Research Laboratory, has been made a Director of Mullard Equipment, Ltd.

MR. VERNON L. FARTHING has been elected Junior Vice-President of the Liverpool Engineering Society, and President of the Liverpool Metallurgical Society.

Owing to rearrangements in the General Engineering Department of Metropolitan-Vickers Electrical Co., Ltd., the following new appointments have been made as from May 1st, 1951. MR. W. ECCLES, hitherto Chief Engineer, General Engineering, has been appointed Chief Engineer, Energy Application Engineering; MR. G. H. JOLLEY, formerly the M-V Export Company's representative in Malaya, is appointed Assistant Chief Engineer of this new department. The old General Engineering Department has been replaced by two new departments, Electrical General Engineering and Mechanical General Engineering. MR. N. R. D. GURNEY has been appointed Chief Engineer, Electrical General Engineering, covering the industrial (including marine), mining and rolling mill sections, MR. W. E. TAYLOR becoming Consulting Engineer, Rolling Mills, in this department. MR. W. J. PRICE is appointed Chief Engineer, Mechanical General Engineering, dealing with power station installations.

The Late Mr. O. H. Wass

We regret to announce the death of Mr. Oswald H. Wass, Chief Sales Representative of General Refractories, Ltd., of Sheffield. Mr. Wass had been with the company since 1924.

LABORATORY METHODS

MECHANICAL · CHEMICAL · PHYSICAL · METALLOGRAPHIC

INSTRUMENTS AND MATERIALS

MAY, 1951

Vol. XLIII, No. 259

The Electrolytic Polishing and Etching of Uranium*

By B. W. Mott and H. R. Haines

Atomic Energy Research Establishment

As a result of a study of electrolytic methods of polishing and etching uranium, the authors suggest a number of suitable solutions, indicating their advantages and limitations.

IN the development of atomic energy, the need for the examination of the structure of uranium in various conditions has assumed importance. In 1946, Chipman¹ drew attention to the difficulties of etching uranium sections to reveal the grain structure, and to the advantages of electrolytic polishing over mechanical polishing. The electrolyte described by Chipman contained 5 parts of orthophosphoric acid, 5 parts of ethylene glycol and 8 parts of ethyl alcohol but no details of the polishing conditions were given. Due to the anisotropy of uranium at room temperature (alpha-uranium is orthorhombic), it is possible to examine the structural characteristics of uranium under polarised light and this was the procedure adopted by the U.S. Atomic Energy Commission after polishing in the above solution. Jacquet² has described the use of an electrolyte containing 20 volumes of acetic acid to 1 volume of perchloric acid and claims that surfaces so prepared are suitable for examination under polarised light.

Solutions Recommended for Electrolytic Polishing

(a) *Apparatus.*—The authors have experimented with the solutions recommended by both Chipman and Jacquet, and also with many others based on the common inorganic and organic acids, and have selected four electrolytes as having a useful application. The apparatus used is essentially the same in all cases, and consists of a glass dish containing the solution, in which is immersed a glass coil of about 12 cm. diameter consisting of 4–6 coils of 1 cm. diameter glass tubing. A continuous stream of cold water is passed through the coil and this has been found to be the most satisfactory method of keeping the solutions cool. The electrodes are placed side by side inside the coil about 4–6 cms. apart, the cathode being of uranium, platinum or stainless steel, in order of preference, and contact being made to the specimen by a steel or platinum wire looped around it, or a pair of stainless steel tweezers if the specimen is small. The circuit normally employed is of the potentiometric type, the current and potential difference across the cell being controlled by a variable resistance.

(b) *Perchloric acid solutions.*—Polishing in all perchloric

acid solutions results in some preferential attack on uranium surfaces, and specimens prepared in this way are never free from imperfections. The rate of polishing depends on the orientation of the grain, so that some grains in a multigrained specimen will stand out in relief and the surface will be uneven. The amount of grain relief depends on the polishing time, current density and the difference in orientation between adjacent grains. In some areas, twin lamellae are also revealed. In addition to the effects due to orientation, perchloric acid attacks any second phase which may be present, such as uranium oxide, U_3Fe , etc. The appearance of a section from a sample of uranium is shown in Fig. 1, in which most of the effects described above may be observed. In some respects, treatment in perchloric acid solutions results in partial etching, which serves to reveal some, but not all, of the grain characteristics of the material, as is shown by a critical examination under polarised light after more suitable preparation.

At A.E.R.E., we have used perchloric acid solutions as a rapid means of removing the effects of cold deformation during surface preparation, e.g., for examination of the structure by back reflection X-ray methods. We prefer to use a more concentrated solution however than that recommended by Jacquet and the two compositions normally employed are as follows:—

Solution A.—Perchloric acid, 60% (density, 1.54).

Solution B.—Perchloric acid, 50 ml. (60% solution).
Glacial acetic acid, 200 ml.

Polishing with solution A is more rapid than with solution B, but a greater degree of control is possible with the more dilute solution. The current density for both solutions must be fairly high and of the order of 1 amp./sq. cm., depending on the shape of the specimen. The time of polishing depends on the concentration of the electrolyte and the original state of the surface being polished, but varies from about 20 seconds, for a surface which has been given a rough mechanical polish on coarse alumina, to about 3 minutes, for one taken down to 00 emery paper.

(c) *Phosphoric acid solutions.*—An investigation of the polishing characteristics of the type of solution described by Chipman¹ has shown that the quality of the polish is not appreciably affected by the relative concentration of its constituents, nor by the substitution of glycerol for ethylene glycol. The solution adopted for our earlier work was of the following composition:—

* Manuscript received December 15th 1950.

¹ Chipman, J., "Metallurgy in the development of atomic power," U.S. Atomic Energy Commission. Publ. M.D.D.C. 539, 1946.

² Jacquet, P. A., and Caillet, R., "Electrolytic polishing of uranium for physico-chemical and metallographic studies," *Comptes Rendus*, **228**, 1949, p. 1224.

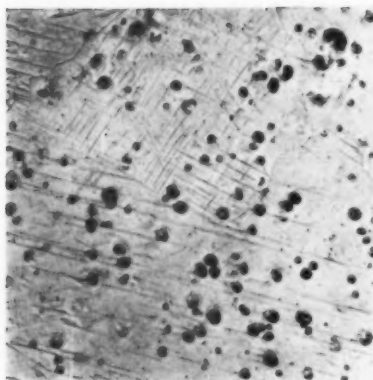


Fig. 1.—Uranium electrolytically polished in perchloric acid. $\times 375$

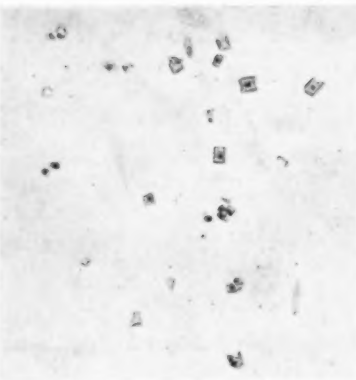


Fig. 2.—Oxide inclusions in uranium electrolytically polished in phosphoric-sulphuric acid solution. $\times 500$

Solution C.—Orthophosphoric acid, 100 ml.
Glycerol, 100 ml.

Ethyl alcohol (absolute), 100 ml.

The optimum current density is from 0.1 to 0.2 amp./sq. cm. and the results are not affected by stirring the solution during polishing. The anodic layer formed at the surface is extremely viscous and precautions must be taken to keep the bath free from water, which results in staining of the surface. For these reasons, the normal procedure is to switch off the current and either leave the specimen in the bath for several minutes, or immerse the specimen immediately in ethyl alcohol to facilitate removal of the anodic layer. It may be necessary to dither the specimen in the alcohol or to wipe the surface gently with a soft brush to speed up the dissolution of the viscous film. Finally, the specimen is washed in a stream of absolute alcohol and dried with a hair dryer in the normal way. The time taken to obtain a satisfactory surface for examination under polarised light is about 5 minutes, if mechanically polished previously, and about 20 minutes if prepared only to 000 emery. The surface so prepared gives far better results when examined under polarised light, since neither the grain boundaries nor metallic impurities are attacked. Prolonged polishing, however, does result in slight attack of the metal in the neighbourhood of oxide particles, and the flatness of the surface deteriorates progressively. For this reason, if a critical examination under polarised light is required, it is preferable to polish the specimen mechanically, prior to electrolytic polishing, to ensure maximum flatness of the surface.

In view of the time taken to give a satisfactory polish and the danger of producing irregularities by prolonged periods of polishing, we have chosen a fourth solution as our standard electrolyte from numerous others which have been tried. The composition of the electrolyte is as follows:—

Solution D

Orthophosphoric acid, 50 ml.

Concentrated sulphuric acid, 100 ml.
Distilled water, 100 ml.

Polishing is carried out at an optimum current density in the range 0.5 to 0.75 amp./sq. cm. and proceeds at an appreciably faster rate than with solution C, although more control is possible than with the perchloric acid solutions. There is a tendency for staining to occur, especially in the earlier stages of polishing, but this can be prevented by stirring the solution or wiping the surface continuously with a brush during polishing. The polished surface obtained is generally very flat and the tendency to pit is far less than with any other solution investigated so far. Due to the increase in the uniformity of the surface, the reaction to polarised

light is more satisfactory than with specimens polished in solution C. The quality of the polish obtained can be judged from Fig. 2, in which the cubic inclusions of UO_2 are clearly revealed without undue attack. Fig. 3 shows the appearance of recrystallised material under polarised light, and reveals deformation twins produced on rapid cooling of the specimen.

Electrolytic Etching

(a) *For microscopical examination.*—The etching of uranium sections for microscopical examination has proved to be most difficult and only one technique has yielded reasonable results, although it is not entirely reliable and, as with the electrolytic polishing in perchloric acid solutions described above, reveals only the more marked differences in orientation. The procedure adopted was to polish the surface in solution C at a current density of about 0.15 amp./sq. cm., remove the anodic film by brushing or immersion in alcohol, then continue the electrolytic treatment for about 8 minutes in the same solution, at about 1/40 of the current density used for polishing, and dry off in the usual way. This procedure resulted in delineation of the grain boundaries and part of the twinning structure, with only a marked difference in intensity



Fig. 3.—Uranium cold-worked and annealed. Electrolytically polished and viewed under polarized light. $\times 100$

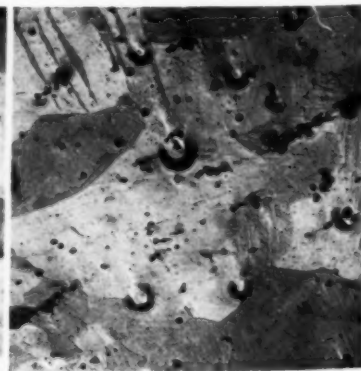
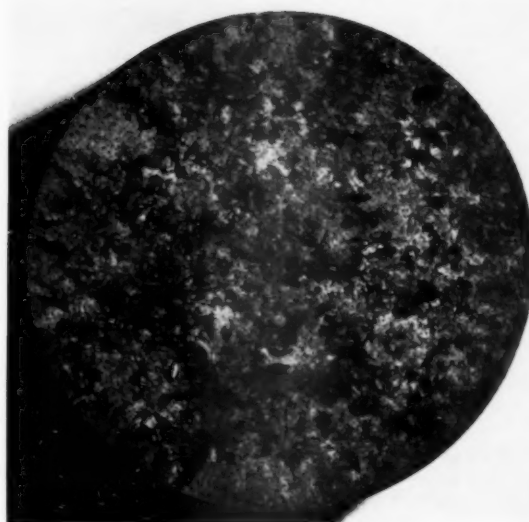


Fig. 4.—As Fig. 3, electrolytically etched and viewed under normal illumination. $\times 110$



Figs. 5a and 5b.—Macrostructure of cast uranium illuminated from different angles.

for grains of markedly different orientation. Fig. 4 shows an area in the same specimen as that used for Fig. 3 and it will be observed that, although the essential features revealed are similar, greater detail is obtainable by the polarised light technique. Etched surfaces have been accidentally obtained on specimens treated by shorting the electrodes, or applying an artificial back E.M.F. to the cell, but the above technique has given the most satisfactory results.

(b) *For macroexamination.*—Various electrolytes may be used for macroetching and the following have all been used successfully in conjunction with the apparatus described for polishing.

Solution C.—As above.

If the etching treatment at about 0.005 amp./sq. cm. is prolonged for about 30 minutes, an etch is obtained which indicates a "macro" grain size.

Solution E.—Orthophosphoric acid, 50 ml.

Water, 450 ml.

The optimum current density for etching is about 0.05 amp./sq. cm. and satisfactory etches are obtained in about 15 minutes under these conditions. Etching occurs, however, at all current densities in the range 0.005–0.5 amp./sq. cm., the lower the current density used, the longer the time required to give sufficient grain contrast.

Solution F.—Citric acid, 50 gm.

Concentrated sulphuric acid, 5 ml.

Water, 450 ml.

The conductivity of this solution is low compared with that of the others described, but satisfactory etches can be obtained by treatment at 0.05 amp./sq. cm. for 30–40 minutes.

Solution G.—Concentrated nitric acid, 50 ml.

Glacial acetic acid, 50 ml.

Water, 400 ml.

Etching occurs in this solution over a wide range of current density, but the most satisfactory results are obtained after about 10 minutes at 0.05–0.1 amp./sq. cm.

Mention may be made of the fact that the size of the grains revealed by macroetching cast material is larger

than that revealed by polarised light, due to the similarity in orientation between adjacent grains. In addition, the appearance of the macrostructure changes with the orientation of the specimen relative to the incident light. This is illustrated by Figs. 5a and 5b which were taken on the same specimen using a single light source at two different angles, as indicated by the shadow, and show the change in the grouping of the grains with the direction of the incident light.

Acknowledgments

The authors wish to record their thanks to the Director, Atomic Energy Research Establishment, Harwell, for his kind permission to publish this article. Thanks are also due to Mr. S. Ford of the Metallography Section and to Mr. D. H. Baker of the Photographic Division for their assistance with the photographs.

French Metallurgical Society Autumn Meeting

THE Société Française de Métallurgie is planning to hold its annual Journées Métallurgiques d'Automne in Paris from October 22nd to 27th, 1951. The meeting will be run on similar lines to the one arranged last October when a large number of specialists from other countries presented papers. The French Society is anxious to have once more the collaboration of scientists from abroad concerned with different problems of metallurgy. Those interested are invited to write to the Société Française de Métallurgie, 5 Cité Pigalle, Paris, 9ème.

Marine Gear Unit Orders

DAVID BROWN & SONS (HUDDERSFIELD), LTD. have received a repeat order for four marine gear units for installation in a fleet of large twin-engine tankers which William Gray & Co., Ltd. are building at West Hartlepool for British and foreign shipping companies. This latest contract brings the number of these David Brown transmission units so far ordered to seven, valued at approximately £150,000. Two of the units, each weighing 52 tons have already been supplied and a third is under construction at Park Works, Huddersfield.

The Study of Dusts in Industrial Atmospheres

3—The Impinger and Cascade Impactor

By P. F. Holt, B.Sc., Ph.D., D.I.C., F.R.I.C.

(University of Reading)

Following his discussion of the use of the thermal precipitator, the konimeter, and the jet dust counter, for the determination of the particle count of a dusty atmosphere, the author now proceeds to deal with the impinger and the cascade impactor. The latter is the most recently introduced apparatus for this purpose and it is considered that it will find wide application in the study of industrial dust problems.

WITH the exception of the thermal precipitator, the apparatus for the estimation of dust particle counts which has been discussed in previous articles has been of a type suitable for taking "snap" samples only. The sampling is completed in, perhaps, a second and it is representative of the state of the atmosphere at a particular instant. The thermal precipitator sample is taken over, say, ten or fifteen minutes and gives a picture of the average dustiness during that period. The impinger is another apparatus designed to take samples over a period and thus to give a measure of the average dustiness of the atmosphere. The air sample is drawn through a jet to impinge on a glass surface under water. The dust is retained as a suspension in the water from which it may be separated

by filtration and weighed or, alternatively, a volume of the suspension is allowed to settle out on a special type of microscope slide and the dust particles are counted.

THE IMPINGER

A diagram of the impinger is shown in Fig. 1. The glass jet, which has an internal diameter of 2.3 mm. and an external diameter of 8 mm. at its tip, is held in a glass outer vessel, 5 cm. in diameter and 30 cm. long, by means of a rubber bung. The vessel contains 100 ml. of water. A rubber collar at the top of the inlet tube prevents loss of dust suspension as spray. Suction is applied to the side tube by means of an ejector, and the air flow is measured with a suitable meter.

Advantages of this impinger are that it is simple and cheap to construct and that air samples of any size can be handled. Until recently it had almost entirely displaced other types of sampling instruments in America, although it was never very popular in this country. Its efficiency increases with the sampling velocity, which is normally about 28 litres per minute. Drinker gave its efficiency as 96% on a silica dust cloud, but Green and Watson found the efficiency much lower. It is usual practice to count

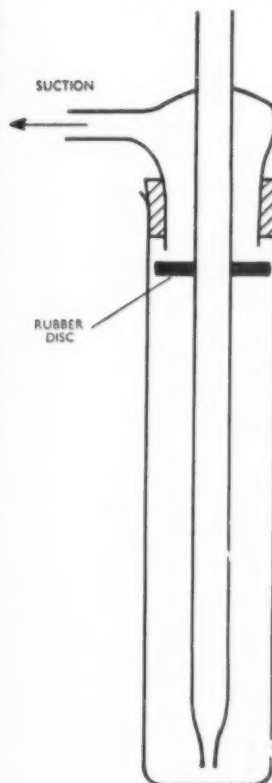


Fig. 1.—The impinger.

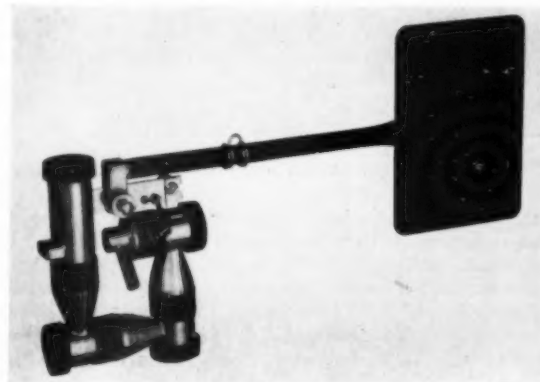


Fig. 2.—The cascade impactor.

impinger samples under low-power magnification ($\times 200$), which means that particles smaller than 0.8 micron are missed. Using this technique, the efficiency of the impinger was found to be about 40%. The use of dark ground illumination can extend visibility to the lower particle sizes but it has been stated that the counts are then less reliable.

THE CASCADE IMPACTOR

An apparatus which has been developed quite recently by the Ministry of Supply, and is finding increasing use in the study of industrial dusts is known as the cascade impactor (Ministry of Supply Patent No. 580705). It was originally designed to sample mist droplets in the size range of 0.5 to 200 microns carried by wind of velocity around 8 m.p.h. It has since been applied to the sampling of all types of aerosols, including dust, and has also been adapted to sample from stationary air.

The principle of the cascade impactor, Fig. 2, is similar to that of the konimeter in that the sample is collected by forcing the air through a narrow jet to impinge on a glass slide coated with a suitable adhesive, but in the impactor the air must pass consecutively through four jets, each of smaller size than the last (Fig. 3). As the air passes through a coarser jet its velocity is less than when it passes a finer jet and, because of this, finer particles are not retained by the earlier coated slides; a size grading of the particles results. This separation is an advantage since it facilitates counting and largely obviates the possibility that a coarse particle may be deposited over and obscure a number of smaller particles.

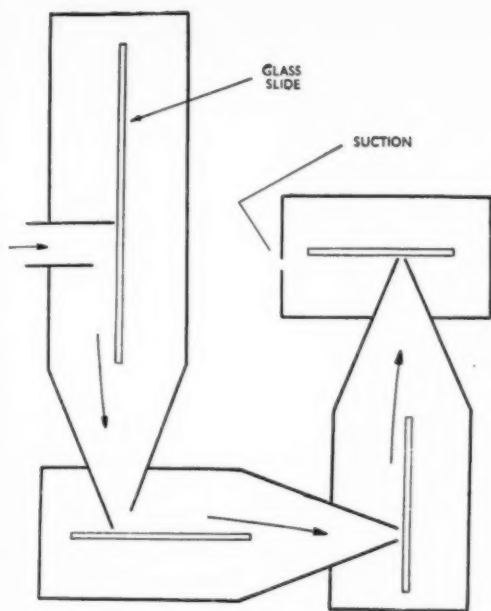


Fig. 3.—Diagrammatic representation of the cascade impactor showing the jet positions.

To a large extent it prevents the coalescing of droplets when mists are sampled.

The apparatus is built in the form shown in the figure and in use it is hung from gallows by a light cord attached at its centre of gravity. A wind vane is built on to the instrument so that it may always orientate itself to ensure that the direction of sampling is the same as the direction of the wind. When sampling from still air, an orifice adaptor is used as otherwise very irregular deposits are obtained on the first slide.

There are several preparations which are satisfactory for coating the slides. These include a mixture of castor oil and high purity rosin, "Vaseline" and polyisobutene; they are applied in chloroform or benzene solution. The necessity for a high purity adhesive must be stressed; unless the rosin, for example, is perfectly clear, dark ground illumination cannot be used for counting.

The size and shape of each jet of the impactor has been designed with special regard to the particle size of dust which is to be collected at that jet and to the velocity of air-flow through the jet. The first jet is 19 mm. wide and has a curved underside, being 7 mm. deep at the centre or 6 mm. deep at the sides; it has a length of 2 cm. and terminates 1 mm. from the collecting microscope slide. This shape is designed to give an even deposit on the slide, and the underside is cut away to terminate 6 mm. from the slide. At a standard sampling rate of 17.5 litres per minute, the air velocity through the first jet is 2.2 metres per second. The remaining jets are rectangular in shape and 14 mm. wide. The second jet is 2 mm. deep, chamfered at 45° and having the lower edge nearly touching the collecting slide. At the standard sampling rate the air velocity through this jet is 10.2 metres per second. The third and fourth jets have slot widths of 0.75 mm. and 0.27 mm. respectively, and the clearance from the slide is in each case identical with the slot width. The sampling velocities at the

standard sampling rate are respectively 27.5 and 77 metres per second. The chamfering of the first two jets ensures that the major part of the airstream turns towards the next jet and so prevents loss of dust in the dead-space between the jets and the casing.

As a source of suction for the cascade impactor it is convenient to use a small motor driven pump or, better still, an injector unit of a type designed to operate on compressed air from a bottle. One such type of injector will provide a flow of 20 litres per minute through the apparatus for an expenditure of about 4 litres per minute of compressed air. The rate of flow through the impactor is best controlled by fitting a critical pressure orifice.

Size segregation in sampling is well illustrated by tests made with heterogeneous spray clouds. It was then found that all particles larger than 20 microns were collected on the first slide, those larger than 7 microns were found on the second whilst particles larger than 2.5 microns were absent from the last slide. This segregation enables counting to be carried out with a different magnification for each slide.

The cascade impactor is the most recently introduced apparatus for the collection of dust particles for the determination of particle count and size distribution. Whilst it has not the same absolute accuracy as the thermal precipitator, it has a number of advantages over other types of dust sampling instruments and it will certainly find a wide application in the study of industrial dust problems.

Norwegian Plant for Disposal

DURING the occupation of Norway by the Germans, a decision was taken by them to develop the Norwegian alumina industry. For this purpose two exceptionally large plants were planned, and chemical and metallurgical equipment of the latest design was sent there just before the end of the war.

Subsequently the ownership of the plant passed to the Norwegian Government, who handed it to A/S Aardal Verk of Norway, the Government-sponsored undertaking controlling aluminium and alumina production in that country.

Recently there has been a re-orientation of the Norwegian alumina industry, which is now concentrating on the manufacture of metallic aluminium. This has released several hundred-thousand pounds worth of first-class equipment, and A/S Aardal Verk have arranged with George Cohen Sons & Co., Ltd., Wood Lane, London, W.12, to co-operate in the disposal of all this equipment.

Particularly at the present time, when urgent requirements for heavy plant are outstripping delivery, it should be of the greatest interest to manufacturers of bulk chemicals, gas and sewage boards, steelworks, glassworks, mines, quarries and cement works, and allied industries.

Most of the plant is unused and much of it has never been erected. Included in the items for disposal are a powder packing plant; gas producer plants; electrostatic precipitators; various types of filters; a rotary kiln; turbo gas compressors; and a selection of elevators, conveyors, screens, separators, etc.

The bulk of the plant is located at Sandasjoen, in S.W. Norway, and the balance at Aardal, to the east of Bergen. At both sites there are deep water berths which will accommodate ships of almost any draught.

Colorimetric Determination of Iron

A Review of Known Methods—2

By T. S. West

Chemistry Department, University of Birmingham

This article is continued from the April issue in which the author discussed the use of ortho-phenanthroline and α , α' diprydil in the colorimetric determination of iron.

Determination with Thiocyanate

The colour reaction between thiocyanate and ferric ions was first observed by Ossian²² in 1837, and Herapath²³ was the first to use it for the colorimetric determination of iron. Since then many workers have adapted the method for special analysis. The chief advantage of the reagent is that it is cheap, and can be used in strongly acid media. The colour depends on the amount of reagent in excess, a large amount favouring colour formation, deepening the intensity, and stabilising the colour against the effects of fluctuation in acidity. It also reduces errors due to the formation of ferric complexes with chloride, phosphate, etc.

There has been some controversy as to the constitution of the ferric-thiocyanate complex. The work of Stokes and Cain²⁴ and Valkenberg²⁵ amongst others, seems to indicate that the coloured ion is $[\text{Fe}(\text{CNS})_6]^{3+}$ but other workers²⁶⁻³⁰ found evidence for the existence of both $[\text{Fe}(\text{CNS})]^{2+}$ and $[\text{Fe}(\text{CNS})]^{+}$.

Zega³¹ found that nitric was more effective than hydrochloric acid for colour formation and this was substantiated by Woods and Mellon³² while Peters and French³³ observed that nitrates generally increase the colour. Phosphate³⁴, sulphate and chloride decrease the intensity, while iodide, nitrite and thiosulphate interfere by their reducing action. Cyanide, citrate and tartrate do not interfere. Dichromate oxidises the reagent and quinquivalent molybdenum develops a colour.

Silver and mercury (I) form insoluble thiocyanates and cadmium, zinc and divalent mercury form colourless complexes with the reagent, and thus interferes by bleaching the colour of the ferri-thiocyanate complex. This bleaching effect cannot be overcome by addition of excess reagent. Coloured ions of course interfere, and in addition copper and cobalt form coloured thiocyanates.

The ferric thiocyanate colour tends to fade rapidly. This is thought to be due to reduction of the ferric iron by thiocyanate or its decomposition products. In diffuse daylight in N/2 hydrochloric acid solution, the colour bleaches 10% over a period of 10 minutes. In nitric acid of the same strength it is found that the colour decreases for 15 minutes, and then increases till it is more intense than the original. This is thought to be due to the formation of a yellow-brown compound between thiocyanate and nitric acid. In order to combat the bleaching effect, attempts have been made to extract the colour with organic solvents or to stabilise it. In the latter category, hydrogen peroxide has been used to oxidise the solution back to its original colour. Peter, MacMasters and French³³ have found it possible to stabilise the colour for several months by addition of sufficient hydrogen peroxide. They stress, however, that addition of too much peroxide may oxidise the thiocyanate, with a resultant increase in colour.

The use of organic solvents to extract the colour was

first examined by Natanson³⁵ who employed ether. This solvent has been used by many workers, and in a recent paper Jones³⁶ has found ether to be superior to isoamyl alcohol, isopropyl alcohol, petroleum ether and chloroform. Not only did ether give the best extraction, but in its solution the thiocyanate complex showed the maximum adsorption, the intensity remaining unchanged over a period of several hours. Three extractions gave virtually complete separation and the extracts could be concentrated without loss of iron. Tarugi³⁷ on the other hand maintains that such extraction is never complete. Other non-miscible solvents which have been used are amyl alcohol,²⁴ ethylene glycol, butyl ethyl ether, diethyl ether and ethyl acetate.

Miscible solvents act by suppressing the ionisation of the coloured complex. Miller, Forbes and Smythe³⁸ used 78% acetone but found that the 22% water was sufficient to dissociate the complex in a short time, and the use of higher proportions of acetone was undesirable due to the insolubility of inorganic compounds in high concentrations of acetone—a flocculent white precipitate being formed by thiocyanate itself. Woods and Mellon³² find that the colour intensity is increased 100% in 60% acetone solution, but Winsor³⁹ in favouring 2-methoxyethanol claims that use of the latter reagent yields a colour that is 85% more intense than the colour in aqueous solution, and 27% more than in the most favourable acetone water mixture. There is also 96% less evaporation than with the aqueous-acetone system. Other workers⁴⁰ have found that ethylene glycol and butyl-ethyl ether dissolved in small amounts in the aqueous solution stabilise the colour sufficiently to permit the colorimetric estimation. In solutions stabilised by addition of a miscible solvent the interference of ions such as phosphate, fluoride, etc., is greatly reduced.

It is common practice to use mixtures of various salts as colour standards. Jackson⁴¹ recommended a mixture of cobaltous chloride and potassium chlorplatinate as suitable, while Velichkovskaya⁴² used cobaltous nitrate and ferric chloride. Others⁴³ have suggested potassium chlorplatinate, cobaltous chloride and cuprous chloride in admixture, and solutions of cobalt amines have also been used.³²

In a recent spectrophotometric study of the ferri-thiocyanate reaction Ovenston and Parker⁴⁴ have found it unnecessary to extract or stabilise the colour with organic solvents. They find that the fading of colour is greatly accelerated by light, and that the stabilising effect of ammonium persulphate is considerable. Wirth⁴⁵ has adapted the thiocyanate method to the determination of iron in the presence of considerable quantities of meta- and pyrophosphate. If an aluminium nitrate reagent is added, the phosphate ions are bound in a complex, and reaction with the ferric ion is inhibited. Brown⁴⁶ has used a two component colorimetric method

for the determination of iron with the thiocyanate reagent in the presence of cobalt.

The thiocyanate reagent is inexpensive, readily available in a pure state, and the reaction is sensitive but the complex is unstable and although capable of partial stabilisation, the colour also depends on the excess of reagent employed. It is possible to use the reagent in 3N acid. Temperature must be fairly closely controlled. Under specified conditions the thiocyanate method is accurate and sensitive, but methods employing ortho-phenanthroline, α , α' dipyridyl and mercapto-acetic acid are generally to be preferred.

Determination with Ferron

Ferron (7-iodo-8-hydroxyquinoline-5-sulphonic acid) was advanced by Yoe⁴⁷ in 1932 as a suitable reagent for the colorimetric determination of ferric iron. The reagent itself has a yellow colour in aqueous solution, and reacts with ferric iron to give a green-blue colour, ferrous ions giving no reaction. The reaction is sensitive, as little as 0.1 p.p.m. giving sufficient colour in a 50 ml. tall-form Nessler tube. The colour is stable over a period of 36 days,⁴⁸ and no variation in colour over the temperature range 10°–40° C. is observed. The most favourable pH range is from 2 to 3. This was confirmed by Swank and Mellon⁴⁹ who state, however, that the pH control must be regulated to within 0.2 unit in contrast to the conclusions of Clark and Sieling,⁵⁰ who found stable colour to exist between pH 2.7 and 3.2.

Yoe and Hall⁴⁸ used a hydrochloric acid, potassium hydrogen phthalate buffer, and in addition Swank and Mellon investigated glycine and sodium acetate buffers, phosphate and citrate buffers being unsatisfactory. They advise adjustment of pH as closely as possible prior to addition of the buffer.

The nature of the colour reaction is unknown, but Yoe and Hall concluded that the complex consists of three ferron molecules and one atom of iron. Although they found that the colour system obeys Beer's law over the range they examined, Swank and Mellon disagree, and claim that the colour depends on the concentration of the reagent, and is, therefore, not directly proportional to the amount of iron present.

Since no other ion gives a green colour with ferron, the reaction is specific. Other ions do interfere, however, although in many cases the interference is a function of the hydrogen ion concentration. Cupric ions form a precipitate, and other ions, such as tin and titanium which readily hydrolyse must be removed. Fluoride, phosphates (pyro and ortho), cyanide, citrate, tartrate and oxalate interfere with full development of colour. Nitrite and pyrophosphate should be totally absent. Copper, nickel and cobalt interfere by consuming the reagent, and since the intensity depends on the concentration of the latter, they interfere although the complexes are colourless. With aluminium and nickel the interference is greater at pH 3 than at 2. Swank and Mellon claim that the effect of interfering elements cannot be overcome by addition of excess reagent. Yoe and Hall state that there is no interference from ferrous iron.

The same workers have adapted the method to the estimation of iron in glass, rocks, clays and alloys such as sheet brass, cast bronze and zinc base die-casting alloy. The elements, copper, tin and antimony were present in all these alloys, and in addition nickel was present in two of them. The brass and bronze were analysed by the method of Lundell and Scherrer.⁵¹ In

the case of the zinc base die-casting alloy only aluminium and copper were present in amounts great enough to make their removal necessary. Low analyses were obtained with the alloys, and this was attributed to the difficulty of the separation of small amounts of iron from large amounts of elements such as antimony, etc. This conclusion is borne out by the work of Goodman,⁵² who obtained low results with the ortho-phenanthroline method in the analysis of brass and bronze. As a result it was found necessary to adopt the procedure of McKay and Ravner⁵³⁻⁵⁴ for solution of the sample, i.e. solution in a mixture of hydrofluoric and nitric acids, and subsequent electrolysis. By this procedure copper and lead are removed.

Swank and Mellon conclude that although the method is a valuable addition to the existing methods for determining iron, it requires careful control of experimental conditions. The colour of the reagent, and the lack of linearity between the colour and the amount of iron present, necessitate the use of a constant-depth technique of comparison.

Determination with Tiron

Tiron (disodium-1, 2-dihydroxybenzene-3, 5 disulphonate) was proposed by Yoe and Jones⁵⁵ as a colorimetric reagent for iron. Large amounts of diverse ions have no effect on the colour produced with ferric iron, but in the presence of 1 p.p.m. of iron the concentration of copper must not exceed 25 p.p.m. and titanium should be absent as it yields a colour with the reagent. The colour developed with ferric iron is an intense blue, the complex consisting of a singly charged anion having the constitution $[\text{Fe}(\text{Tiron})_2]^-$. Variation in pH alters both the intensity and hue of the colour, below pH 5.7 the solution being blue, between 5.7–7 violet, and above 7 an intense red. Yoe and Jones found that the greatest sensitivity is obtained with the red complex at pH 9.5, using a disodium phosphate buffer, though they also used the blue complex at pH 4 with a hydrochloric acid, sodium acetate buffer.

Colour standards of both complexes, once prepared, are stable for several months, after an initial increase in colour over the first 18 hours. The reagent is specific for iron, no other ion giving a red colour. Molybdate, copper (II), uranium (UO_2), vanadate and titanium also yield coloured complexes. The colour with titanium is intense, the reagent being more sensitive for this metal than for iron. Along with molybdenum and copper, however, titanium can readily be removed by means of hydrogen sulphide.

The reagent is colourless, highly soluble in water and produces no change in the intensity of the coloured solution of the ferric complex, even when a large excess is present. By utilisation of the red complex which is completely stable in alkaline medium, it is possible to determine iron in the presence of large amounts of fluoride, tartrate, oxalate, citrate and phosphate. This is impossible with most of the other reagents that have been used for the colorimetric determination of ferric iron. In the presence of strong oxidising agents, such as perchloric acid, the reagent may become oxidised to a darkish-coloured solution. Beer's law is valid for both complexes within the range 0.2–10 p.p.m. With the red complex it is possible to estimate visually with a 50 ml. tall-form Nessler tube as little as 1 part in 200,000,000 and with the blue complex 1 part in 30,000,000.



Marshall

REFRACTORIES



In addition to the normal properties expected of a good refractory—Casting Pit Ware must be accurate in shape and size to ensure good joints and close fittings in the Trumpet Casing and Runner Channel. These illustrations show examples of what we have in mind. Latest production methods and control ensure the right qualities in every piece. Continuous research and development to improve such products is part of our policy.

Marshall

THOMAS MARSHALL & CO. (LOXLEY) LTD.

STORRS BRIDGE WORKS
LOXLEY N^o. SHEFFIELD

PHONE: SHEFFIELD
43844/5

GRAMS: MARSHALL
LOXLEY SHEFFIELD

Greenburgh⁵⁶ has adapted the method to the determination of small quantities of iron in substances containing relatively large amounts of arsenic, antimony, copper and nickel. Sufficient reagent is added to cover all the nickel, copper and ferric iron present, and a sodium carbonate bicarbonate buffer is employed. The determination must be made within four minutes of adding the buffer. Beer's law was found to hold for iron and nickel, but a substantial divergence occurs in the presence of copper, though a correction can readily be applied. Armstrong and Potter⁵⁷ have applied the reagent to the simultaneous determination of titanium and iron in cathode nickel.

Determination with Salicylic Acid

The amethyst colour produced by reaction of salicylic acid with ferric iron in acetic acid medium has been known for a long time but not until 1907 was it used to estimate iron.⁵⁸ The method has since been used by many workers, and its limitations have been indicated. Snell⁵⁹ and Yoe⁶⁰ report that all the common mineral acids interfere as do phosphate thiosulphate, bisulphite and fluoride while other workers⁶¹ state that citrate oxalate and tartrate must be absent.

The colour system obeys Beer's law up to an iron content of 20 mg. per litre, and Bech⁶² states that the optimum pH is 2.2 while Mehlig⁶³ found it to be 2.6-2.8. An ammonium acetate buffer is used, and the adsorption is measured at 520 m μ . A large excess of the reagent must be avoided as it generates a brownish colour. Yoe⁶⁰ states that the colour fades rapidly in bright light, Snell⁵⁹ found it to be stable for 48 hours under ordinary laboratory conditions, and Mehlig⁶³ claimed the colour was stable for 66 hours. In all cases, bright sunlight was found to accelerate the fading.

On account of their reducing action or complexing powers, a number of common anions cause a decrease in the intensity of the colour. In the first category are sulphite, iodide and thiosulphate whilst in the latter are found arsenate, tungstate and cyanide. Nitrite forms a greenish colour with the reagent and thiocyanate and iodide should be entirely absent. Some cations form coloured complexes while others, such as aluminium, form colourless complexes, which lead to a diminution in the intensity of the colour produced by ferric iron. Copper, cobalt, nickel, chromium, uranium and manganese alter the hue of the solution.

In the analysis of copper alloys, Gregory⁵⁸ removed the blue colour due to copper, by adding potassium cyanide, but excess cyanide must be avoided as it causes a diminution in the colour due to iron. Other cations form precipitates or turbid solutions and altogether it is found that because of their interference, a considerable number of ions have to be removed from solution prior to the determination of iron.

Determination with Sulphosalicylic Acid

In acid medium, ferric iron reacts with sulphosalicylic acid to yield a red colour, similar to that obtained by reaction of thiocyanates with iron, the colour reaction being about equally as sensitive.⁶⁴ In alkaline solution the reagent reacts with ferrous and ferric iron to produce a yellow colour, the presence of oxidising agents turning the yellow colour to brown. Hence the reagent may be employed for the determination of both forms of iron. According to Lorber⁶⁵ however, the depth of colour produced by ferric iron in acid solution is decreased by

the presence of ferrous iron, although a correction can be applied.

An iron concentration of 1-20 mg. per litre is reported by Kennard and Johnson⁶⁶ to be the most suitable range. Measurement of the adsorption at pH 8.2 gives the maximum sensitivity, but the widest range of iron concentrations is covered at pH 1.5. Rosanov et alia^{67,72} report the method of Alten, Wieland and Hille,⁶⁴ for the determination of iron, to be unsuitable in the presence of large amounts of phosphate, but by omitting the addition of the citrate buffer and by increasing the concentration of the reagent to five times that originally specified, it is possible to determine one part of Fe₂O₃ in the presence of 100 parts of P₂O₅.

Aluminium, calcium, silicon do not interfere, but the presence of ferrous ions is objectionable. Kennard and Johnson found that phosphate interferes at pH 5, but overcame the difficulty by applying a correction. Chloride and nitrate do not interfere, but large amounts of copper, nickel and cobalt do, due to formation of a deep green or brown colouration with the reagent. Cyanide may be added to complex the copper.

Urech⁶⁸ has used the sulphosalicylic acid method for the determination of iron in aluminium alloys by colorimetric titration. Thiel and Van Hengel⁶⁹ compared the sulphosalicylic acid with the α , α' dipyridyl and 7-iodo-8-hydroxyquinoline methods, and reported that best results were obtained with the first reagent. This judgment is confirmed also by Wenger and Duckert⁷⁰ who found a 5% aqueous solution of sulphosalicylic acid to be the most superior reagent. Benze⁷¹ on the other hand preferred ortho-phenanthroline.

The sulphosalicylic acid reagent has been used to determine iron in apatites,⁶⁷ phosphates⁷² and other phosphates,⁷³ chrome plating baths,⁷⁴ aluminium alloys⁷⁵ and aluminium,⁷⁶ magnesium alloys,⁷⁷ boric acid and borax^{78,79}.

Determination with Salicylaldoxime

The colour imparted to a solution of ferric iron by salicylaldoxime was first noted by Ephraim.⁸⁰ The reagent forms insoluble inner complex compounds with many metals, and has been used in the gravimetric estimation of copper, nickel, lead and palladium. The iron complex, however, is soluble and Ephraim originally used a solution of ferric iron to test the washings of his copper and nickel precipitates in order to determine when the precipitate had been washed free of the reagent. Howe and Mellon⁸¹ reversed this procedure, and used the salicylaldoxime as a means of determining iron.

The colour developed at pH 3 is purple, and at pH 10, becomes yellow. Mellon and Howe worked at pH 7, at which level the colour was found to be stable for over 24 hours. The maximum colour develops in 30 minutes and the use of excess reagent is permissible. In acid solution the colour develops instantaneously, but fades rapidly; in alkaline solution the time of development is 15 minutes. The maximum adsorption is found at 480 m μ and one part of iron in 20,000,000 parts of solution can be detected in a 30 cm. Nessler tube.

Chloride, bromide, thiocyanate, chlorate, perchlorate, sulphate and acetate do not interfere, but fluoride, citrate, tartrate, oxalate, cyanide, borate, phosphate and carbonate do. Few of the colourless cations interfere. Lead, zinc, mercury, beryllium and aluminium have no effect, if sufficient reagent is added to complex them. The reagent does, however, form a yellow solution with

molybdate, and intensifies the colour of cobalt solutions.

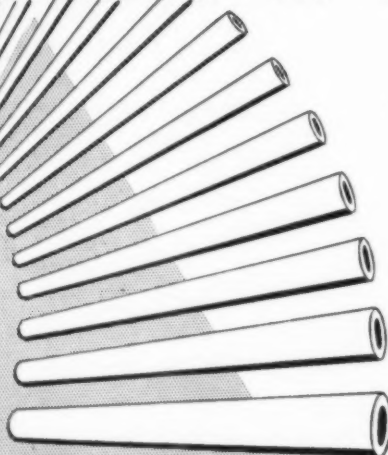
Howe and Mellon conclude that the reagent is sensitive, that the colour system obeys Beer's law, and although the colour is only stable for 24 hours this is normally sufficient. The reagent is readily available and inexpensive, and can be used for the routine determination of copper and nickel. Although the control of pH is critical it is not more so than in the ferron method.

REFERENCES

- 22 Ossian, H., *Pharm. Centr.*, 1837, **13**, 205.
- 23 Herapath, T. J., *J. Chem. Soc.*, 1855, **5**, 27.
- 24 Stokes, H. N., and Cain, J. B., *J. Am. Chem. Soc.*, 1907, **29**, 409.
- 25 Schlosinger, H. L., and Valkenberg, H. B., *ibid.*, 1951, **53**, 1212.
- 26 Møller, Kern, *Mannedblad.*, 1937, **18**, 138.
- 27 Bent, H. E., and French, C. L., *J. Am. Chem. Soc.*, 1941, **63**, 568.
- 28 Edmonds, S. M., and Birnbaum, N., *ibid.*, 1941, **63**, 1471.
- 29 Gould, R. K., and Vosburgh, W. C., *ibid.*, 1942, **64**, 1630.
- 30 Frank, H. S., and Oswalt, R. L., *ibid.*, 1947, **69**, 1321.
- 31 Zega, A., *Chem. Zeit.*, 1893, **17**, 1564.
- 32 Woods, J. T., and Mellon, M. G., *Ind. Eng. Chem. Anal.*, 1941, **13**, 551.
- 33 Peters, C. A., MacMaster, M. M., and French, C. L., *ibid.*, 1939, **11**, 502.
- 34 Moore, T., *Chem. News*, 1886, **53**, 209.
- 35 Natanson, J., *Ann.*, 1861, **130**, 246.
- 36 Jones, F., *Anal. Chem.*, 1949, **21**, 1216.
- 37 Tarugi, N., *Ann. Chim. Applicata*, 1926, **16**, 281.
- 38 Miller, R. C., Forbes, E. B., and Smythe, C. V., *J. Nutrition*, 1929, **1**, 217.
- 39 Winsor, H. W., *Ind. Eng. Chem. Anal.*, 1937, **9**, 453.
- 40 Rakistrow, N. W., Mahniker, H. E., and Beach, E. T., *ibid.*, 1936, **8**, 136.
- 41 Jackson, S. H., *Tech. Quart. M.I.T.*, 1909, **13**, 329.
- 42 Velichkovskaya, T. D., *J. Applied Chem. (U.S.S.R.)*, 1939, **12**, 1425.
- 43 Hallinan, F. J., *Ind. Eng. Chem. Anal.*, 1943, **15**, 510.
- 44 Ovenston, T. C. J., and Parker, C. A., *Anal. Chim. Acta.*, 1949, **3**, 277.
- 45 Wirth, H. E., *Ind. Eng. Chem. Anal.*, 1942, **14**, 722.
- 46 Brown, E. A., *ibid.*, 1945, **17**, 228.
- 47 Yoe, J. H., *J. Am. Chem. Soc.*, 1932, **54**, 4139.
- 48 Yoe, J. H., and Hall, R. T., *ibid.*, 1937, **59**, 872.
- 49 Swank, H. W., and Mellon, M. G., *Ind. Eng. Chem. Anal.*, 1937, **9**, 453.
- 50 Clark, N. A., and Sieling, D. H., *ibid.*, 1936, **8**, 236.
- 51 Lundell, G. E. F., and Scherrer, J. A., *Ind. Eng. Chem.*, 1922, **14**, 426.
- 52 Goodman, W., *Ind. Eng. Chem. Anal.*, 1947, **19**, 141.
- 53 McKay, L. W., *J. Am. Chem. Soc.*, 1909, **31**, 578.
- 54 Ravner, H., *Ind. Eng. Chem. Anal.*, 1945, **17**, 41.
- 55 Yoe, J. H., and Jones, A., *ibid.*, 1941, **16**, 111.
- 56 Greenburgh, R. H., *ibid.*, 1946, **18**, 255.
- 57 Armstrong, C. E., and Potter, C. V., *Anal. Chem.*, 1948, **20**, 1208.
- 58 Gregory, A. W., *J. Chem. Soc. Trans.*, 1908, **93**, 93.
- 59 Snell, F. D., and C. T., "Colorimetric Methods of Analysis," N.Y., D. van Nostrand Co., 1936, p. 301.
- 60 Yoe, J. H., "Photometric Chem. Analysis, I," N.Y., Wiley & Sons, 1928, 244.
- 61 Sugaldachnui, A., and Ravich, M., *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 1018.
- 62 Bech, P. F., *Dansk. Tids. Farm.*, 1935, **9**, 289.
- 63 Mehlig, J. P., *Ind. Eng. Chem. Anal.*, 1938, **10**, 136.
- 64 Alten, F., Wieland, W., and Hille, E., *Z. Anorg. Chem.*, 1935, **215**, 81.
- 65 Lorber, L., *Biochem. Z.*, 1927, **181**, 391.
- 66 Kennard, M., and Johnson, C. R., *Proc. Trans. Ter. Acad. Sci.*, 1944, **27**, 45.
- 67 Rozanov, S. N., Markova, G. A., and Fedotova, E. A., *Z. Pflanz. Ung. Bodenk.*, 1955, **41**, 59.
- 68 Urech, F., *Helv. Chim. Acta.*, 1939, **22**, 322, 331.
- 69 Thiel, A., and Van Hengel, P., *Re. r.*, 1937, **70B**, 2491.
- 70 Wenger, P., and Duckert, R., *Helv. Chim. Acta.*, 1944, **27**, 757.
- 71 Benze, B., *Mezgapzhazagi Kutatask.*, 1941, **16**, 61.
- 72 Rozanov, S. N., Markova, G. A., and Fedotova, E. A., *Zur. Lab.*, 1935, **4**, 638.
- 73 Peshkova, V. M., and Egorov, A. D., *Zarodskaya Lab.*, 1935, **4**, 885.
- 74 Pfeiffer, H., *Z. Anal. Chem.*, 1943, **129**, 81.
- 75 Bauer, R., and Eisen, J., *Angew. Chem.*, 1939, **52**, 459.
- 76 Khinov, L., and Arnold, T. L., *Zarodskaya Lab.*, 1943, **3**, 894.
- 77 Nikitina, E. L., *Zarodskaya Lab.*, 1943, **3**, 629.
- 78 Zussner, E. E., *ibid.*, 1939, **8**, 112.
- 79 Zussner, E. E., *Khim. R. Fort. Zhv.*, 1940, **4**, 51.
- 80 Ephraim, F., *Re. r.*, 1939, **64B**, 1928.
- 81 Howe, D. E., and Mellon, M. G., *Ind. Eng. Chem. Anal.*, 1940, **12**, 448.

TUBES in Standard sizes

Suitable
thermocouple
insulators
available



'TRIANGLE' RECRYSTALLISED ALUMINA
Formerly 'Triangle RR'

'TRIANGLE' IMPERVIOUS MULLITE
Formerly 'Triangle HS'

We are preparing stocks of the following
range of standard sizes:—

Diam. in mm.			
Outside	Inside	Outside	Inside
8 × 5		48 × 40	
14 × 10		59 × 50	
20 × 15		70 × 65	
31 × 25		86 × 75	

* Recrystallised Alumina only

Available in lengths:—

Recrystallised Alumina up to 900 mm.
Impervious Mullite up to 1,200 mm.

THE MORGAN CRUCIBLE COMPANY LIMITED

BATTERSEA CHURCH ROAD · BATTERSEA · LONDON S.W.11

TELEPHONE BATTERSEA 8822

TELEGRAMS CRUCIBLE, SOUPHONE, LONDON
CL.100

in
the
the
the

IA

E

g

e

ly

W
00